A Study of the Preparation and Reactions of Titanium(IV) Carboxylate Species

by

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Declaration

The work herein reported was carried out between October 1990 and September 1993 in the Department of Chemistry at Warwick University, and in the Propathene Catalyst and Development laboratory at I.C.I. Wilton.

Part of the work concerning the species $[\{TiCl_2(O_2CR)(RCO_2H)\}_2O]$ (R=Me, CMe_3) reported in this thesis has been previously published:

Hazel Barrow, David. A. Brown, Nathaniel W. Alcock, Howard J. Clase and Malcolm G. H. Wallbridge, *J. Chem. Soc., Dalton Trans.*, 1994, 195.

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ABBREVIATIONS

acac	Acetylacetonate anion
acacen	N, N' ethylenebis(acetylacetone iminato)dianion
bipy	2, 2'-bipyridyl
Cp	Cyclopentadienyl
Cp'	Methylcyclopentadienyl
Cp*	Pentamethylcyclopentadienyl
diket	β-diketonate anion
DME	Dimethoxyethane
dmpe	Dimethylphosphoethane
$HBpz_3$	Tri-1-pyrazolylborate ion
HMPA	Hexamethylphosphoric triamide
py	Pyridine
Salen	Bis(salicylaldehyde)ethylenediimine
TACN	1,4,7-Triazacyclononane
Me_3TACN	1,4,7-Trimethyl-1,4,7-triazacyclononane
THD	2,2,6,6-Tetramethyl-3,5-heptanedionate anion
THF	Tetrahydrofuran
EC180	Hydrocarbon solvent, mixture of dodecanes, b.p.180°C
Me	Methyl
Et	Ethyl
Pr	Propyl
Bu	Butyl
Ph	Phenyl
b.p.	Boiling point

ABBREVIATIONS continued.

NMR	Nuclear magnetic resonance	IR	Infra-red
δ	Chemical shift	w	Weak intensity
J	Coupling constant	m	Medium intensity
s	Singlet	s	Strong intensity
d	Doublet	sh	Shoulder
t	Triplet	asym	Asymmetric
q	Quartet	sym	Symmetric
m	Multiplet	br	broad
brs	Broad singlet		
brm	Broad multiplet		

Abstract

This thesis describes the preparation and structural features of a number of titanium(IV) carboxylate species. The compounds $[Ti_2Cl_7(O_2CR)(RCO_2H)]$ (R=Et, CMe_3) and $[\{TiCl_2(O_2CR)(RCO_2H)\}_2O]$ (R=Me, Et ***1***, CMe_3 ***2***, C_6F_5, $CH_2C_6F_5$) have been synthesised by the addition of $TiCl_4$ to the respective carboxylic acid at 25°C. For R=C_6F_5 and $CH_2C_6F_5$, no 1:1 species could be isolated. Structure elucidation of the compounds ***1*** and ***2*** has revealed that they contain the $[Ti(\mu_2\text{-}O)(\mu_2\text{-}O_2CR)_2Ti]^{4+}$ core. The propanoate derivative may also lose a further mole of HCl on leaving the reaction solution for 4 days to give $[Ti_2OCl_3(O_2CEt)_3(EtCO_2H)]$. A second form of the pentafluorophenylacetate derivative has been isolated which appears to contain both bridging and terminal chlorine atoms in addition to unidentate and bidentate carboxylate ligands. However, ^1H NMR experiments indicate that in solution both forms are identical. Carrying out the reaction of $C_6F_5CH_2CO_2H$ with $TiCl_4$ in chloroform (stabilised with ethanol) gives a hexanuclear species of the formula $[Ti_6O_4Cl_2(OEt)_6(O_2CCH_2C_6F_5)_8]$ which has been fully characterised by X-ray structural studies.

The acid $C_6F_5OCH_2CO_2H$ reacts with $TiCl_4$ at room temperature to produce a compound of the formulation $[\{TiCl_2(O_2CCH_2OC_6F_5)\}_2O]$ in which the ethereal group of the carboxylate ligand co-ordinates to the metal. This latter compound and species of the type $[\{TiCl_2(O_2CR)(RCO_2H)\}_2O]$ (R=Me, Et, CMe_3) react with tetrahydrofuran to give $[\{TiCl_2(O_2CR)THF\}_2O]$. X-ray crystal structure determination has shown that $[\{TiCl_2(O_2CCH_2OC_6F_5)THF\}_2O]$ has a structure analogous to ***1*** and ***2***. Controlled hydrolysis of $[\{TiCl_2(O_2CCMe_3)THF\}_2O]$ produces the tetramer $[\{TiOCl(O_2CCMe_3)THF\}_4]$ which has been structurally characterised.

Heating ***1*** and ***2*** in light petroleum at 60°C and 40°C respectively produces the trimeric compounds $[Ti_3O_2Cl_3(O_2CR)_5]$ (R=Et ***3***, CMe_3) which contain both μ_2-O and μ_3-O bridges as shown by X-ray structure studies of ***3***. Further high temperature reactions utilising $C_6F_5CO_2H$ and $C_6F_5CH_2CO_2H$ have given products of a different stoichiometry, namely $[TiO(O_2CR)_2]$. Structure determination of $[TiO(O_2CC_6F_5)_2]$ has shown it to comprise of a sixteen membered ring of titanium and oxygen atoms. In contrast, the reaction of $TiCl_4$ with $C_6F_5OCH_2CO_2H$ at high temperatures is proposed to give the compound $[Ti_3O_2Cl_4(O_2CCH_2OC_6F_5)_4]$.

A small number of aluminium carboxylate species of the formulation $[AlCl_2(O_2CR)]$ (R=Et, CMe_3), $[AlCl(O_2CEt)_2]$ and $[Al(OH)(O_2CPh)_2]$ have been synthesised and characterised by elemental analysis, IR and ^1H NMR spectroscopy.

Finally, the results of solution and heterogeneous catalytic tests on some of the titanium carboxylate species are reported.

CHAPTER ONE

INTRODUCTION

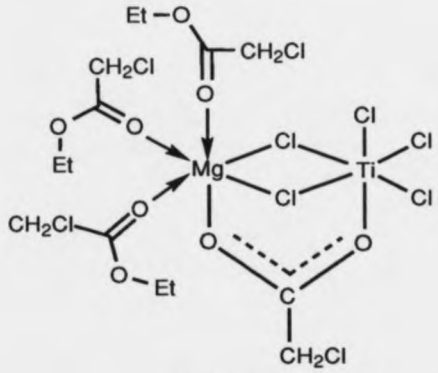
1. INTRODUCTION

One of the most spectacular chemical discoveries of the 1950's was made by Ziegler and co-workers who demonstrated catalysts that were able to polymerise ethylene at room temperature and low pressures.[1] In collaboration, Natta and co-workers modified these catalysts to produce stereoregular polymers of a high molecular weight from many olefinic hydrocarbons.[2]

As originally described, Ziegler-Natta catalysts consist of the combination of a transition metal compound with an organometallic compound of groups 1, 2 or 13, the most successful results originating from the association of titanium compounds with aluminium alkyls.

Modifications of this basic catalyst have led to an improved yield and stereoregularity of the polymer.[3] One such alteration was the loading of the catalyst onto an inert support. Many of these supported catalysts are used in industry today and are often comprised of a magnesium chloride support with an aromatic ester and titanium tetrachloride.[4] The active catalyst is then produced by treatment with a trialkylaluminium combined with another aromatic ester. Although several Lewis bases have been used in these catalysts, stereospecificity in particular is only achieved using aromatic esters.[5] Detail will be paid to the design of these systems in Chapter 7.

The development of the large scale commercial supported catalyst increased research at a molecular level into the $MgCl_2$ / $TiCl_4$ / ester system, with the aim of understanding the chemical bonding and possibly identifying the active site in the supported catalysts. The reaction product of titanium tetrachloride, magnesium chloride and ethyl chloroacetate has been structurally characterised as $[TiMgCl_5(O_2CCH_2Cl)(ClCH_2COOC_2H_5)_3]$ **(1.1)** and found to contain magnesium and titanium centres.[6] The $TiCl_4$ receptor molecule has changed its co-ordination from tetrahedral to octahedral, while $MgCl_2$ has maintained, unaltered, its octahedral co-ordination.



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The two metals are joined by a triple bridge composed of two chlorine atoms and a chloroacetate ion, the latter being produced by cleavage of some of the ethyl chloroacetate ester during the reaction. This structural model showed the possibility that carboxylate bridges may be present in the ester-containing supported Ziegler-Natta catalytic systems, and the added possibility that this structural feature may play a part in the formation of the active site.

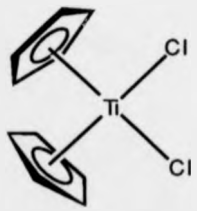
In collaboration with I.C.I., a research programme was set up involving the preparation and study of titanium compounds containing carboxylate ligands. For this thesis, novel titanium(IV) carboxylate species have been prepared and subsequently tested for their catalytic properties in supported systems. It is envisaged that catalytic analyses of a large number of these titanium carboxylate species could prove a useful aid in the further development of commercial supported catalysts.

The following introductory chapter aims to highlight some of the chemistry and structural features of titanium compounds and will, by necessity, be selective. Further to this, we shall see the versatility of carboxylic acids as ligands, and also how the study of the vibrational spectra of metal carboxylate species can act as an aid in the assignment of carboxylate bonding modes.

1.1 Titanium and its Compounds

Titanium is in Group 4 of the periodic table and is an early transition metal element. In line with its outer electronic configuration of $3d^24s^2$ its maximum and also its most stable valence is 4, but lower oxidation states of 3, 2, 0, -1 and -2 have also been found in its complexes.[7] With few exceptions, the organic complexes of lower valent titanium are extremely sensitive to oxygen. In many cases oxidation is so rapid that the compounds are pyrophoric in air.

The organometallic chemistry of titanium is extensive and several detailed reviews can be found on this subject.[8] Many compounds have been isolated, most of these containing the cyclopentadienyl (Cp, C_5H_5) ligand. The subject is of major importance owing to the facility with which certain organotitanium compounds catalyse the polymerisation of α-olefins using Ziegler-Natta catalysis.[3,9] The red, crystalline titanium(IV) derivative, $[Cp_2TiCl_2]$ **(1.2)** has a tetrahedral structure.[10] It has an extremely varied chemistry involving reduction to Ti(III) and Ti(II) species, and is the principal starting material for much of the reported organometallic chemistry. Recent interesting developments have involved the use of *ansa*-metallocenes for the stereoregular polymerisation of α-alkenes.[11]



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Another very important and widely used starting material is titanium(IV) chloride, $TiCl_4$. It is a colourless, distillable liquid which behaves as a Lewis acid, forming a wide range of addition compounds. $TiCl_4$ can also react with many compounds containing active hydrogen atoms such as hydroxy (OH) groups, with the loss of HCl. The general methods of preparation and the chemistry of the halides of titanium have been reviewed

by Clark.[7] The properties of the halides vary widely as the oxidation state of the titanium changes; the tetrahedral monomeric tetrahalides $TiCl_4$, $TiBr_4$ and TiI_4 are without oxidising or reducing properties but the hexa-co-ordinate halogen-bridged halides of titanium(III) and (II) have reducing properties, especially the dihalides.

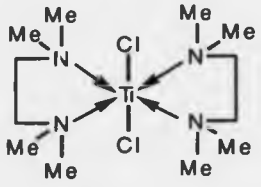
The chemistry of titanium and its compounds can be widely found in inorganic textbooks and in general reviews.[7,12] As an introduction to this thesis, discussion will be centred on the co-ordination chemistry of titanium(IV) halides, chiefly with oxygen donor ligands. The chemistry of the lower valent halides will be briefly acknowledged.

1.2. Titanium(II) Halides and their Co-ordination Chemistry

$TiCl_2$, $TiBr_2$ and TiI_2 are black crystalline solids while TiF_2 is only known in the gaseous state. All have strong reducing properties, shown by their ability to liberate hydrogen from water, and may be prepared by disproportionation of the respective trihalide.[7] Common ligands (e.g. pyridine) do not easily break up the lattice, and consequently, reactions are often carried out at high temperatures, in sealed tubes, or with refluxing for long periods.

Direct reaction of $TiCl_2$ with certain ligands, although slow, has given adducts formulated as $[TiCl_2.2L]$ (L=dimethylformamide, acetonitrile) which have been assigned polymeric structures with halogen bridges.[13] Displacement of acetonitrile from $[TiCl_2.2MeCN]$ allows a successful preparation of further adducts, for example $[TiCl_2.2L]$ (L=pyridine, tetrahydrofuran, tetrahydropyran) and $[TiCl_2.L]$ (L=2,2'-bipyridyl, 1,10-phenanthroline).[14]

Recent X-ray structural characterisation of the tetramethylethylenediamine (TMEDA) adduct of titanium(II) chloride, $[TiCl_2.2TMEDA]$ **(1.3)**, has revealed an octahedral monomeric species with the chlorine ligands *trans* to each other.[15] Other derivatives of titanium(II) include $[Ti(dmpe)_2Cl_2]$[16] and $[Ti(O_2C_5H_7)_2]$,[17] and the dialkylamido compounds $[Ti(NR_2)_2]$ (R=Me, Et and ^iPr).[18]



(1.3)

1.3. Some Chemistry of the Titanium(III) Halides

The titanium(III) halides are all crystalline solids at room temperature with strong reducing properties and have a polymeric structure involving halogen bridges with titanium in an octahedral environment. They disproportionate or sublime at high temperatures and, with the exception of TiF_3, are oxidised in air at 25°C.[19]

Various preparative methods for the trihalides are known. Commonly, TiX_3 (X=F, Cl, Br, I) are prepared by reduction of the corresponding tetrahalide with titanium metal at 600°C, although the temperature and time varies for each trihalide. Alternatively, to prepare the trichloride and tribromide, the appropriate tetrahalide may be reduced by hydrogen gas.[7]

$$2TiCl_4 + H_2 \xrightarrow{800°C} 2TiCl_3 + 2HCl$$

Complexes of titanium(III) are usually formed by direct reaction between the trihalide and an excess of the ligand. The derivatives produced are unstable towards air and also usually towards moisture.

Primarily, $TiCl_3$ has been used in the preparation and research of titanium(III) species, and its co-ordination chemistry is dominated by titanium occupying an octahedral environment. The octahedral titanium(III) ion is a d^1 system and generally the magnetic moments of Ti(III) complexes are all near the expected value of 1.73BM at room temperature.

Many complexes of different stoichiometries are known for the addition compounds of the trihalides, e.g. $[TiX_3L_3]$, $[TiX_3L_2]$, $[TiX_2L_4]^+X^-$, $[TiL_6]^{3+}3X^-$

(X=F, Cl, Br, I; L= monodentate ligand) and many compounds are known in which bi- and ter-dentate ligands are co-ordinated to the metal atom. A summary of the range of addition complexes with titanium(III) halides is given in Table 1.1.

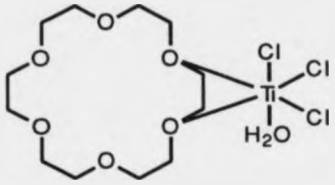
Table 1.1 Addition products of titanium(III) halides.

Complex	Structure	Example	Ref.
$TiX_3.L_3$	*Fac*-octahedral	X=Cl, L=MeCN, HMPA	20, 21
	Mer-octahedral	X=Cl, L=THF, C_5H_5N	22, 23
$TiX_3.L_2$	*Trans*-trigonal bipyramidal	X=Cl, Br, L=NMe_3	24
	Octahedral through halogen bridges	X=Cl, L=SMe_2, C_5H_5N	25, 26
$TiX_3.T$	*Fac*-octahedral	X=Cl, T=$N(CH_2CH_2NMe_2)_3$, $O(CH_2CH_2OMe)_2$, $NMe(CH_2C_5H_3MeN)_2$	27 28 29
$[TiX_2.B_2]^+[TiX_4.B]^-$	*Cis*-octahedral for both ions	X=Cl, B=bipy; X=Br, B=DME	30, 31
$[TiB_3]^{3+}3X^-$	Octahedral cation	X=Cl, B=ethylenediamine, propylenediamine	32 32
$[TiL_6]^{3+}3X^-$	Octahedral cation	X=Cl, L=H_2O; X=I, L=$OC(NH_2)_2$ $X=I_3$, L=MeCN	33, 34 35
$[TiL_4X_2]^+X^-$	*Cis*-octahedral cation	X=Cl, L=$HOCH(Me)_2$; $X=I_3$, L=MeCN, C_5H_5N	36 37, 38
L=Monodentate ligand; B=Bidentate ligand; T=Terdentate ligand			

Treatment of $[TiCl_3.3MeCN]$ with tetraethylammonium chloride produces the ionic species $[Et_4N]^+[TiCl_4.2MeCN]^-$. X-ray analysis of the THF derivative and $[C_5H_6N]^+[TiCl_4.2C_5H_5N]^-$ has confirmed the anion is *trans*-octahedral. Further reaction of $[Et_4N]^+[TiCl_4.2MeCN]^-$ on heating gives the species $[Et_4N]^+[TiCl_4]^-$ with the loss of acetonitrile. Treatment of $[TiCl_3.3MeCN]$ with excess pyridinium chloride gives the salt $[C_5H_6N]_3^+[TiCl_6]^{3-}$ which is solvated in solution to $[TiCl_4L_2]^-$.[39]

Hexa-co-ordination of titanium in the adducts of σ-phenylenebis-(dimethylarsine) with $TiCl_3$ and $TiBr_3$ has been achieved by the formation of monohydrates, for example

$[TiCl_3.C_6H_4(AsMe_2)_2.H_2O]$.[40] This is also seen in the 18-crown-6 adduct $[TiCl_3(18\text{-crown-6}).H_2O]$ **(1.4)**.[41]



(1.4)

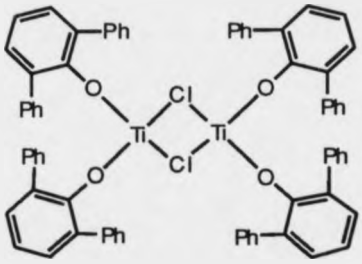
Ligands with replaceable H atoms, or their salts, can react with $TiCl_3$ to form complexes with the liberation of HCl or chloride ions. Reaction of β-diketones with $[TiCl_3.3THF]$ gives the octahedral $[Ti(diket)Cl_2(THF)_2]$.[42] Titanium tris-acetylacetonate has been prepared from the reaction of the ligand with $TiCl_3$.[43] All the tris-β-diketonates are intensely coloured and monomeric, and tris-acetylacetonate has been found to show a strong trigonal distortion.[44]

The structural chemistry of the titanium(III) alkoxides is dominated by the formation of polynuclear molecular clusters with bridging alkoxide groups.

$$TiCl_3 + 3LiOMe \xrightarrow[\text{methanol}]{\text{anhydrous}} [Ti(OMe)_3]_n + 3LiCl$$

The yellow-green tris-methoxide, prepared by the equation above, is diamagnetic due to the strong magnetic interaction between the metal atoms,[45] and its reaction with $TiCl_3$ has produced the mono- and disubstituted derivatives $[TiCl_2(OMe).2MeOH]$ and $[TiCl(OMe)_2.MeOH]$.[46] Higher homologues of $[Ti(OR)_3]$ have been obtained by reduction of the corresponding tetra-alkoxides by sodium or potassium metal.[47]

Recent structure elucidation of the dimer $[\{TiCl(2,6\text{-}OC_6H_3Ph_2)_2\}_2]$ **(1.5)** has shown the titanium atoms to be both four co-ordinate in a distorted tetrahedral environment, and joined by chlorine bridges.[48] The product was prepared by the reduction of $[TiCl_2(2,6\text{-}OC_6H_3Ph_2)_2]$ with sodium amalgam.



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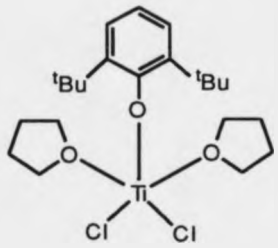


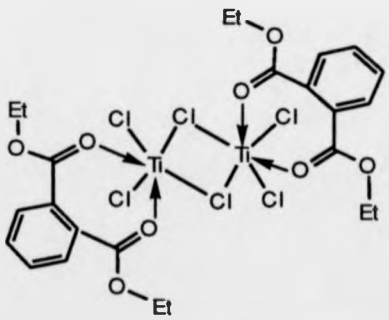
(1.6)

In comparison, a five co-ordinate monomer, $[TiCl_2(2,6\text{-}OC_6H_3{}^tBu_2)(THF)_2]$ **(1.6)**, has been structurally characterised by Floriani *et al* from reaction of the monomeric adduct $[TiCl_3.3THF]$ with 2,6-*di-tert*-butylphenol.[49]

The direct reaction of titanium(IV) chloride, diethyl-*o*-phthalate and metallic aluminium, produced a titanium(III) chloroester species by reduction, as shown in the equation below.[50]

$$6TiCl_4 + 2Al + 8C_6H_4(CO_2Et)_2 \xrightarrow{CH_2Cl_2}$$
$$3[Ti_2(\mu\text{-}Cl)_2Cl_4\{o\text{-}C_6H_4(CO_2Et)_2\}_2]\ 4CH_2Cl_2\ \textbf{(1.7)} + 2[AlCl_3.C_6H_4(CO_2Et)_2]$$

The brown air-sensitive titanium(III) product **(1.7)** is a chlorine-bridged dimer.



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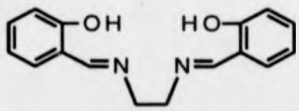


(1.8)

Titanium(III) Schiff-base ligand species have been prepared but despite the potential of these ligands there has been relatively little work done on these systems. Both $[\{TiCl(salen)(C_5H_5N)\}THF]$[51] and $[TiCl(salen)THF]$[52] contain hexa-co-ordinate

titanium with salen **(1.8)** in the equatorial plane and chlorine and pyridine (or THF) mutually *trans*.

The only well established oxyhalide of titanium(III) is TiOCl. It may be prepared by heating the trichloride (in excess) with the dioxide at 650°C for 12 hours in a silica tube *in vacuo*, as shown in the equation below.[53]

$$2TiCl_3 + TiO_2 \longrightarrow 2TiOCl + TiCl_4$$

1.4. Titanium(IV) Halides and their Chemistry

The tetrahalides, especially the tetrachloride and the tetrabromide, are all powerful Lewis acids and form a very extensive series of addition compounds with neutral donors (Lewis bases).[7] Most research has centred on the chemistry of $TiCl_4$, but it has been found that $TiBr_4$, and to a lesser extent TiF_4 and TiI_4, form addition compounds which are isostructural to those of the tetrachloride.

Titanium tetrachloride is prepared by treating titanium dioxide with chlorine gas in the presence of a reducing agent.[54]

$$TiO_2 + 2Cl_2 + 2C \xrightarrow{1000°C} TiCl_4 + 2CO$$

The remaining halides may be prepared from titanium tetrachloride and the appropriate hydrogen halide.[7]

$$TiCl_4 + 4HX \longrightarrow TiX_4 + 4HCl$$

(X=F, Br, I)

Some properties of titanium tetrahalides are shown in Tables 1.2 and 1.3. All the tetrahalides are extremely hygroscopic. Indeed, $TiCl_4$ fumes copiously in air and reacts vigorously with water to produce titanium dioxide.

$$TiCl_4 + 2H_2O \longrightarrow TiO_2 + 4HCl$$

Due to this hydrolysis, reactions of titanium tetrahalides must be carried out in a dry, inert atmosphere.

Table 1.2 Physical properties of the titanium tetrahalides.

Compound	Colour and physical state (r.t.)	M.p.(°C)	B.p.(°C)	Structure*
TiF_4	White crystalline solid	-	284 (subl)	Fluorine bridged polymer
$TiCl_4$	Colourless liquid	-24.1	136.45	Tetrahedral monomer
$TiBr_4$	Orange crystalline solid	38.25	233.45	Tetrahedral monomer
TiI_4	Dark brown solid	155	377	Tetrahedral monomer
* Data from ref. 55				

Table 1.3 Structural parameters for $TiCl_4$ and $TiBr_4$*

Molecule	Molecular symmetry	Ti-X (Å)*	X-Ti-X (°)*	Ref.
$TiCl_4$	T_d	2.170 ± 0.002	109.5	56
$TiBr_4$	T_d	2.31 ± 0.02	109.5	57
* Obtained from electron diffraction data				

Titanium(IV) is a d^0 system and therefore the titanium(IV) halides and other derivatives containing only titanium(IV) centres, are diamagnetic.

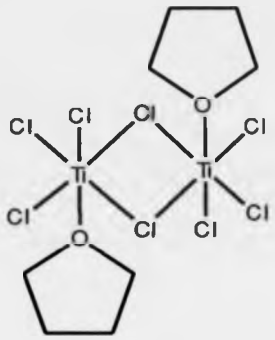
Addition Compounds of Titanium Tetrachloride

$TiCl_4$ forms adducts with nitrogen, oxygen, phosphorous, sulphur and arsenic donor ligands, the majority having titanium in an octahedral environment. However, coordination numbers of 5, 7 and 8 have also been cited.[7]

1.4.1. $TiCl_4$ Adducts with Monodentate Donor Ligands

1:1 Adducts giving [$TiCl_4$.L] (L=Monodentate Ligand)

A large number of these adducts have been fully characterised by X-ray diffraction, namely where L= $POCl_3$,[58] $MeNO_2$,[59] $N{\equiv}CCO_2Et$,[60] $MeOC_6H_4CO_2Et$,[61] $S_3N_2O_2$,[62] $MeCO_2Et$.[63] In these compounds the titanium is in an octahedral environment by dimerisation through halogen bridges as shown for the THF adduct **(1.9)**.[64]



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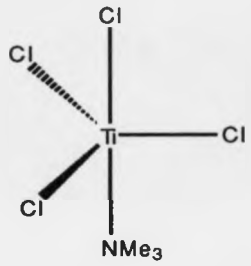


(1.10)

For this type of adduct two types of metal-chlorine stretching vibrations are evident in the IR spectra of these compounds, namely Ti-Cl terminal stretches which occur in the region 450-350cm^{-1} and Ti-Cl-Ti bridging vibrations which can be found at lower frequencies of 300-200cm^{-1}.[65]

One notable exception to the dimeric formulation is the trimethylamine adduct [$TiCl_4.NMe_3$] **(1.10)** whose monomeric unit contains five co-ordinate trigonal bipyramidal titanium.[66] It is proposed that the large bulk of this ligand is a key factor in this anomaly. Absorption bands assigned to Ti-Cl stretching vibrations were observed in the IR spectrum at 457, 396 and 345cm^{-1}, thus indicating the presence of only terminal chlorine atoms.

1:2 Adducts giving [$TiCl_4$.2L] (L=Monodentate Ligand)

These addition compounds are well documented and several adducts have been structurally characterised revealing monomeric, hexa-co-ordinate titanium species with the donor ligands in a *cis* environment, namely where L= $POCl_3$,[67] MeCN,[68] HCN[69] and Et_2O.[70]

While the *cis* configuration is seen in the majority of cases , the *trans* structure is also possible. ^{19}F NMR studies of the derivatives [TiF_4.2L] has given support to the *cis* configuration, showing two signals due to the significant difference in the shielding of the two fluorine environments. Additionally, research with larger ligands has shown that the possibility of obtaining the *trans* form tends to increase as the bulkiness of the ligand increases. It has been possible to isolate the *trans* configuration of [$TiCl_4.2C_5H_5N$],[71] which was subsequently characterised by X-ray diffraction. [$TiCl_4.2PhCO_2Et$] also has *trans* stereochemistry.[72]

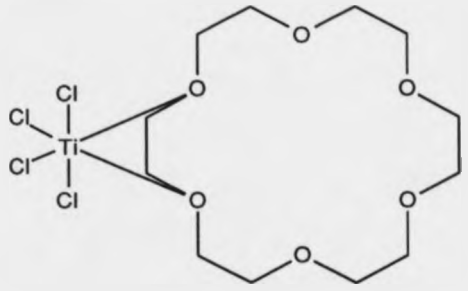
With some ligands, such as $POCl_3$, complexes with both stoichiometries are known which have been identified by X-ray diffraction,[58,67] however, other ligands such as ketones and acid halides appear to form 1:1 adducts exclusively. Clearly there is a fine balance involving both steric and electronic effects which influence the stoichiometry, and also the structure, in the formation of 1:1 and 1:2 adducts.

1.4.2. $TiCl_4$ Adducts with Bidentate Donor Ligands

1:1 Adducts giving [$TiCl_4$.B] (B=Bidentate Ligand)

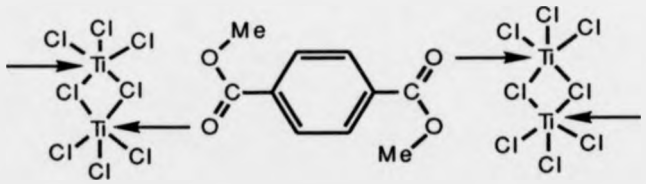
The resulting adduct is generally monomeric with the titanium in an octahedral environment in the majority of cases, as shown by the X-ray data obtained for these systems with ligands such such as $B=Me_2C(COMe)_2$,[73] *o*-$C_6H_4(CO_2{}^tBu)_2$,[74] $O(COMe)_2$.[75]

The cyclic ether 18-crown-6 has been shown to act as a bidentate donor with $TiCl_4$, to give the adduct [$TiCl_4$(O,O-18-crown-6)] **(1.11)**.[76]



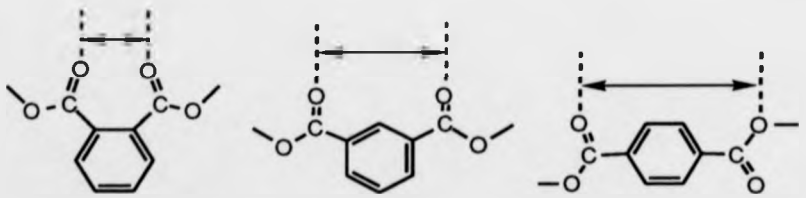
(1.11)

Meta-aromatic diester adducts have recently been structurally characterised, and contain hexa-co-ordinate titanium centres due to dimerisation through diester bridges. Examples of these systems include $[Ti_2\{\mu\text{-}m\text{-}C_6H_4(CO_2CH_2CH_2Ph)_2\}_2Cl_8]$[77] and $[Ti_2\{\mu\text{-}m\text{-}C_6H_4(CO_2Et)_2\}_2Cl_8]$.[78] In the case of the *para*-aromatic diesters, it appears that a polymeric species is obtained, as was shown by X-ray structural analysis of $[Ti_2(\mu\text{-}Cl)_2\{\mu\text{-}p\text{-}C_6H_4(CO_2Me)_2\}Cl_6]_n$ **(1.12)**.[74]



(1.12)

The structures of the adducts of *o*-, *m*-, and *p*-aromatic diesters with $TiCl_4$ contrast sharply, and are in line with the increase in distance between the two donor oxygen atoms as shown graphically below.



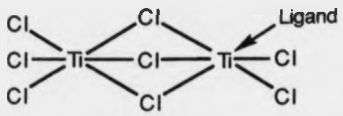
o-diester
Bidentate chelate monomer

m-diester
Bridging dimeric

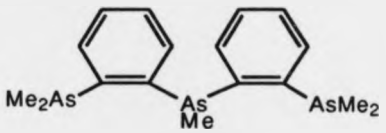
p-diester
Bridging polymeric

1.4.3. Other Adducts with $TiCl_4$

Compounds of the type $[(TiCl_4)_2.L]$ have been reported for $L=MeCO_2C_5H_{11}$, $MeCO_2C_6H_{13}$, $C_4H_9CO_2Et$, $C_5H_{11}CO_2Et$, $C_6H_{13}CO_2Et$,[79] and $OP(NMe_2)_3$ (HMPA)[21] which have a confacial bioctahedral structure **(1.13)**, proposed on the basis of the IR spectra, as both bridging and terminal Ti-Cl stretches were assigned. The ^{31}P, ^{13}C and ^1H NMR spectra of $[(TiCl_4)_2.HMPA]$ were close to those observed for $[TiCl_4.2HMPA]$ and the ligand was assigned as being terminal.[21]



(1.13)



(1.14)

Higher co-ordination numbers of seven or eight for the titanium atom may be exhibited in $TiCl_4$ adducts. Terdentate arsine ligands such as methyl-bis(*o*-dimethylarsinophenyl)arsine **(1.14)**, can give seven co-ordinate monomeric adducts.[80] ^1H NMR experiments demonstrate that all three arsenic atoms of each ligand are co-ordinated to the metal.

With the bidentate ligand *o*-phenylene-bis(dimethylarsine), $TiCl_4$ may form a 1:1 adduct $[TiCl_4.B]$, and a 1:2 adduct $[TiCl_4.2B]$. The 1:2 adduct has been crystallographically characterised by X-ray analysis and $[TiCl_4.2C_{10}H_{16}As_2]$ shows the relatively rare dodecahedral co-ordination around the metal centre.[81] In comparison, the ethyl analogue of the diarsine forms only a 1:1 six co-ordinate monomeric adduct, presumably due to steric factors.

Titanium(IV) Compounds from $TiCl_4$

1.4.4. Titanium(IV) Alkoxides

As well as forming neutral adducts, $TiCl_4$ reacts with a variety of compounds with the replacement of one or more chlorine atoms. The best studied group of

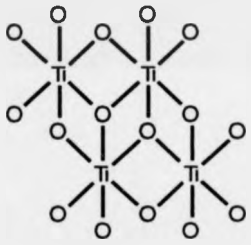
titanium(IV) compounds is the alkoxides. The definitive review of this area is that of Bradley.[82] Two general preparative routes for tetra-alkoxides are available.

(a) $TiCl_4 + 4NaOR \xrightarrow[\text{alcohol}]{\text{appropriate}} [Ti(OR)_4] + 4NaCl$ (slow)

(b) $TiCl_4 + 4ROH + 4NH_{3(\text{anhydrous})} \longrightarrow [Ti(OR)_4] + 4\,NH_4Cl$

(R=alkyl, aryl)

Generally method (b) is employed although in the absence of a reagent which will remove the HCl, the reaction only proceeds as far as the $[TiCl_2(OR)_2]$ derivative. The alkyl systems $[Ti(OMe)_4]$,[83] $[Ti(OEt)_4]$[84] and $[Ti(OMe)(OEt)_3]$[85] have all been isolated and structurally characterised; they are tetrameric in the solid state. These compounds have a $[Ti_4O_{16}]$ **(1.15)** framework and contain hexa-co-ordinate titanium.



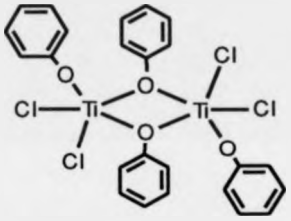
(1.15)

In solution, the lower alkoxides have been found to be trimeric, but if sterically hindered by a large alkyl group then they are proposed to be monomeric. Because of this, the phenoxides, for example $[Ti(OPh)_4]$, readily form 1:1 adducts but the alkoxides $[Ti(OR)_4]$ (R=Me, Et) do not.[86] This difference in behaviour towards Lewis bases is undoubtedly related to the monomeric and therefore co-ordinatively unsaturated nature of the phenoxides in solution, in contrast to that of the alkoxides. The crystal structure of the adduct $[Ti(OPh)_4.PhOH]$ shows it to be a dimer of octahedrally co-ordinated alkoxytitanium molecules.[87]

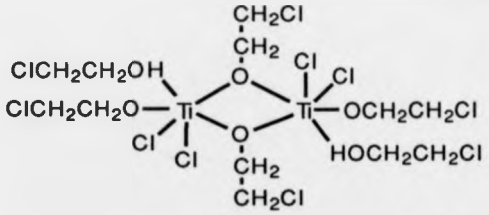
The lower chain alkoxides are rapidly hydrolysed by moist air, but higher homologues, and the phenoxides, are much less susceptible. With carefully controlled conditions it is possible to isolate polymerisation intermediates such as $[Ti_6O_4(OEt)_{16}]$[88]

and $[Ti_7O_5(OEt)_{19}]$.[89] Klemperer and co-workers have carried out controlled hydrolysis reactions to give the polyalkoxides $[Ti_7O_4(OEt)_{20}]$, $[Ti_8O_6(OPh)_{20}]$ and $[Ti_{10}O_8(OEt)_{24}]$ which have been characterised by crystal structure determinations.[90]

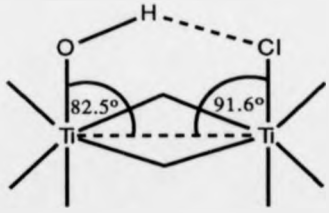
A range of $[TiX_{4-n}(OR)_n]$ compounds (R=alkyl, alkenyl, cycloalkyl, aryl; X=halogen ; n=1,2,3) is known, all of which are hygroscopic. The compounds $[TiCl_2(OPh)_2]$ **(1.16)**[91] and $[TiCl_2(OEt)_2]$[92] have been structurally characterised by X-ray diffraction. Both are dimeric and contain penta-co-ordinate titanium in a trigonal bipyramidal environment. These compounds are generally prepared by direct reaction between the parent tetra-alkoxide and the appropriate molar proportion of the tetrahalide.



1.16



1.17



1.18

The titanium chloride alkoxide of the formula $[\{TiCl_2(OCH_2CH_2Cl)_2(ClCH_2CH_2OH)\}_2]$ **(1.17)** is dimeric with hexa-co-ordinate titanium atoms.[93] Intramolecular OH---Cl hydrogen bonding is present based on the X-ray data **(1.18)**, and this is corroborated in the IR spectrum by the presence of a medium intensity broad hydroxyl band at 3215cm^{-1}, whereas free OH groups generally exhibit a weak, sharp absorption between 3580 and 3650cm^{-1}. The complex was prepared at low temperature from a mixture of $TiCl_4$ with excess 2-chloroethanol.

The use of sterically demanding ligands is now well established as a means of obtaining co-ordinatively unsaturated complexes. The past few years has shown an increase in the phenoxide chemistry of $TiCl_4$ with a resultant expansion of the structural data in this research area. Some compounds which have been fully characterised are shown in Table 1.4.

Table 1.4 Phenoxide compounds of titanium(IV)

Compound	Coord.no.	Ref.
$[TiCl\{N(SnMe_3)_2\}(2,6\text{-}OC_6H_3Ph_2)_2]$	4	94
$[TiI(2,6\text{-}OC_6H_3{}^tBu_2)_3]$	4	95
$[TiCl_2(2,6\text{-}OC_6H_3Ph_2)_2]$	4	94
$[TiCl_2(2,6\text{-}OC_6H_3Me_2)_2(THF)_2]$	6	96
$[TiCl_2\{(OC_6H_2{}^tBuMe)_2CH_2\}]$	4	97

1.4.5. Titanium(IV) Carboxylates

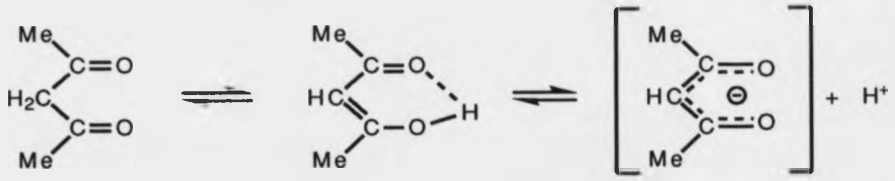
$TiCl_4$ is known to react with aryl and alkyl monocarboxylic acids to produce substituted species with the elimination of hydrogen chloride gas, as shown by the following example equation,

$$TiCl_4 + PhCO_2H \xrightarrow{70°C} [TiCl_3(O_2CPh)] + HCl$$

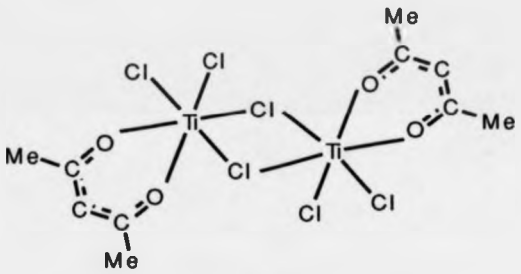
These reaction products will be discussed in greater detail in Chapter 2.

1.4.6. Titanium(IV) β-Diketonates

The most commonly used of this class of bidentate chelate ligand is acetylacetone which forms an anion as a result of enolisation and ionisation, as shown in the scheme below, to form very stable complexes with most metal ions.



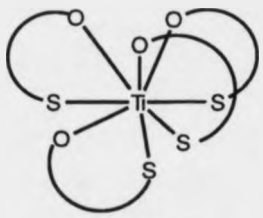
Trichloro(acetylacetonato)titanium(IV) **(1.19)** has been fully characterised from X-ray diffraction studies.[98] It is dimeric in the solid state and is been prepared by the direct reaction of $TiCl_4$ with acetylacetone in a 1:1 molar ratio. In the IR spectrum, the υ(Ti-Cl) were assigned to bands at 378 and 389cm^{-1} (terminal), and 268 and 230cm^{-1} (bridging). The disubstituted product $[TiCl_2(acac)_2]$ has been prepared and assigned a *cis* configuration.[99]



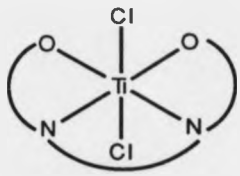
(1.19)

1.4.7. Other Chelates of Titanium(IV)

The reaction of $TiCl_4$ with sodium dimethyldithiocarbamate gives the products $[TiCl_{4-n}(S_2CNMe_2)_n]$ where n depends upon the molar quantity of $[NaS_2CNMe_2]$ used.[100] The products range from six (octahedral) to seven (trigonal bipyramidal) and eight (dodecahedral) co-ordinate for n = 2, 3 and 4 respectively based on molecular weight measurements. X-ray diffraction data for $[TiCl(S_2CNMe_2)_3]$ has confirmed the seven co-ordinate structure postulated. An analogous range of compounds $[Ti_{4-n}(OSCNR_2)_n]$ have been isolated,[101] and the dodecahedral $[Ti(OSCNEt_2)_4]$ has been shown to consist of an all *cis* structure with four sulphur atoms on one side of the co-ordination group and the four oxygen atoms on the other side **(1.20)**.[102]



(1.20)



(1.21)

Schiff bases, for example salen **(1.8)**, react with $TiCl_4$ to give complexes **(1.21)** such as that shown above with the titanium having octahedral symmetry and the chelating ligand lying in the equatorial plane.[103]

1.4.8. Hydrolysis of Titanium(IV) Halides

As previously discussed $TiCl_4$ is readily hydrolysed. If aqueous HCl is used, the oxydihalide $TiOCl_2$ may be isolated as a yellow hygroscopic powder, insoluble in polar solvents and therefore presumed polymeric. The remaining titanium oxydihalides are prepared similarly. $TiOCl_2$ has the ability to behave as a Lewis acid, forming adducts of the type $[TiOCl_2.2L]$ (e.g. L=C_5H_5N, $POCl_3$) which are assigned as having polymeric structures. The oxydichloride decomposes at 180°C to give $TiCl_4$ and TiO_2 (anatase).[7]

Titanium(IV) oxide, TiO_2, is very stable, insoluble in water and involatile. It occurs naturally in three crystalline modifications; rutile, anatase and brookite, the most common of which is rutile. All may be prepared synthetically.

It is an amphoteric oxide, reacting with both acids and bases:

$$TiO_2(H_2O)_n \xrightarrow{\text{conc. } H_2SO_4} TiOSO_4(H_2O)_n \quad \text{Titanyl sulphate}$$

$$TiO_2(H_2O)_n \xrightarrow{\text{conc. NaOH}} Na_2TiO_3(H_2O)_n \quad \text{Sodium titanate}$$

1.5. Metal Carboxylate Species

Having discussed some of the basic aspects of the chemistry of titanium(IV) chloride, it is now essential to look closely at the organic ligands used in this thesis, namely carboxylic acids.

Amongst the three important groups (i.e. alkoxides, β-diketonates and carboxylates) of organic derivatives of metals with metal-oxygen-carbon bonds, metal carboxylates have been known longest . The oldest derivatives are the alkali metal carboxylates, commonly known as 'soaps'. These soaps are soluble in water, with which they readily produce 'foam'. Despite their very long history, the interest in the chemistry of metal carboxylate species is still evident by numerous publications.

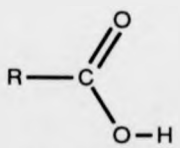
We begin with the structural aspects of these ligands, and view the nature of the bonding involved in their inorganic compounds.

1.6. Carboxylic Acids as Ligands

The Structural Aspects and Physical Properties of Carboxylic Acids

Monocarboxylic acid complexes have occupied a central position in co-ordination chemistry from the 19th century through to the present day. The carboxylate ion is a ubiquitous ligand with a versatile co-ordination behaviour.

A monocarboxylic acid is an organic compound which contains one carboxyl group; the latter itself containing a carbonyl group and a hydroxyl group **(1.22)**.



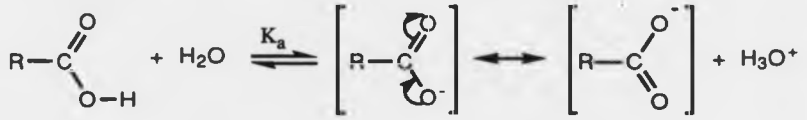
(R=H, alkyl or aryl)

(1.22)

The carboxy group may carry a substituent, R, which influences the properties of the acid. In comparison with mineral acids ($pK_a \leq 1$) carboxylic acids are weak acids

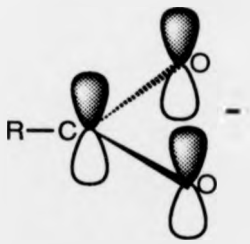
having a pK_a in the range 4 - 5. However, they are more acidic than alcohols or phenols primarily because of resonance stabilisation of the carboxylate anion.

Acidity depends on the degree of ionisation of carboxylic acid into the carboxylate anion and a hydrated proton as shown in the scheme below.



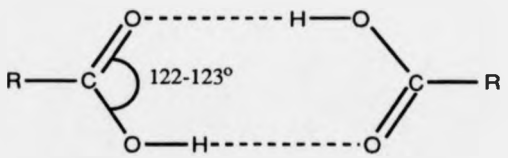
$$pK_a = - \log_{10} K_a$$

The negative charge on the anion is evenly distributed and the carbon-oxygen bond lengths are identical. The carbon atom is sp^2 hybridised and therefore σ bonded to the three adjacent nuclei. In the anion the central carbon is held more tightly to the two oxygen atoms by π bond formation due to p orbital overlap, making the bonds stronger and the anion more stable **(1.23)**.



Side view of p orbital overlap

(1.23)



C=O	1.23Å
C–O	1.36Å
OH···O	2.60-2.70Å

(1.24)

If the substituent R is electron withdrawing, the negative charge of the anion is dispersed, the anion is stabilised, and the pK_a is lowered, thus increasing the acid strength. If R is electron releasing, inductive effects cause the anion to be destabilised, and the acid to have an increased pK_a.

In the solid state, X-ray diffraction has shown a cyclic dimeric structure **(1.24)**. This is also found in the vapour state or in non-ionising solvents. In aqueous solution carboxylic acids tend to dimerise openly in a linear array.

The characteristic stretching frequencies of carboxylic acids in the IR are given in Table 1.5.

Table 1.5 Major absorption bands of carboxylic acids in the IR spectrum

Absorption Band	Frequency
Broad O-H stretch	3300-2500cm^{-1}
Dimeric carboxylate C=O stretch	1715cm^{-1}
C-O-H in-plane bend	1408cm^{-1}
C-O stretch, dimer	1280cm^{-1}
O-H out-of-plane bend	930cm^{-1}

In the ^{1}H NMR of the carboxylic acids, the hydroxyl proton is normally broad and appears at a low field (10-13ppm). It is exchangeable with D_2O and is therefore easily detected. In the ^{13}C NMR spectra of the aliphatic acids, the carbonyl carbon atom resonates at approximately 170-180ppm.

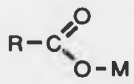
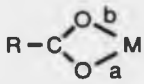
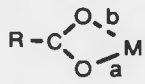
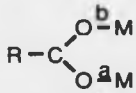
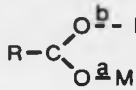
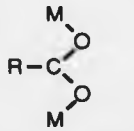
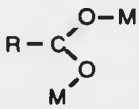
1.7. The Nature of Carboxylate Co-ordination

The carboxylate ion, has the ability to co-ordinate to metals in a number of ways. Three structural co-ordination types have been identified; unidentate, chelating and bridging (Table 1.6).

In addition to co-ordinated derivatives, ionic metal carboxylates are well established, having a symmetrical structure in which the metal atom is associated equally with the two oxygen atoms and the O-C-O angle varies from 100-130°.

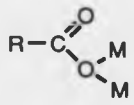
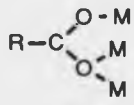
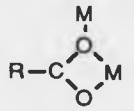
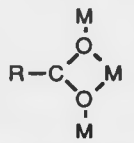
The most extensively investigated co-ordination mode is the bridging system and four types of bidentate bridge have been identified, as shown in Table 1.6. The strong bridging tendency of carboxylate ligand is reflected in the common occurrence of polynuclear carboxylate species.[111]

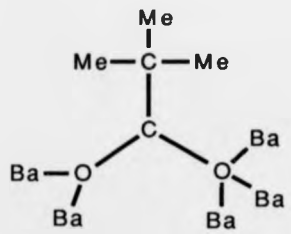
Table 1.6 Unidentate, chelating and bridging carboxylate co-ordination.

Structural Type	Representation	Characterised Example	Ref.
(A) **Unidentate**		$[Ni(O_2CMe)_2(H_2O)_4]$	104
Chelating			
(B) Symmetrical a = b		$[Zn(O_2CMe)_2.2H_2O]$	105
(C) Unsymmetrical a ≠ b		$[Sn(O_2CMe)_4]$	106
Bridging			
(D) *Syn-Syn* Symmetrical a = b		$[Zn_4O(O_2CMe)_6]$	107
(E) *Syn-Syn* Unsymmetrical a ≠ b		$[Sn(CH_2Ph)_3(O_2CMe)]$	108
(F) *Anti-Anti*		$[Cu(O_2CH)_2.4H_2O]$	109
(G) *Anti-Syn*		$[SnMe_3(O_2CMe)]$	110

Mention should also be made of the monatomic carboxylate bridge which is often found in alkoxide chemistry. The monatomic mode (Table 1.7) may act as a bridging ligand alone (H), with additional bridging involving the second oxygen atom (I), or in arrangements involving chelation and bridging (J and K). A recent example of the monatomic bridge is the crystal structure elucidation of the penta-nuclear chelate $[Ba_5(THD)_9(O_2CCMe_3)]$ which has shown the pivalate ion to be bonded to all five barium atoms; one oxygen is bidentate, the other is terdentate as shown diagramatically in **(1.25)**.[116]

Table 1.7 Monatomic carboxylate co-ordination modes.

	Representation	Characterised Example	Ref.
(H)		$[Hg(O_2CMe)_2\{(C_6H_{11})_3P\}]$	112
(I)		$[Cu(O_2CMe)]$	113
(J)		$[Cd(O_2CMe)_2(H_2O)_2]$	114
(K)		$[TlMe_2(O_2CMe)]$	115



(1.25)

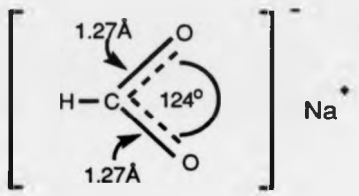
Definitive information concerning the co-ordination mode of the carboxylate ion can only be achieved by diffraction studies, but many structures have been postulated from spectroscopic techniques such as IR and NMR. Unfortunately, these latter methods have, on occasions, resulted in inaccurate assignments.

With such a large number of metal carboxylate structures characterised by diffraction studies, some correlation of structural and IR data has been possible. As the C-O stretching frequencies are usually the most prominent feature of the vibrational spectrum, attention has naturally focused upon this particular mode and upon its possible

application in the assignment of the specific carboxylate co-ordination modes.[117] The following section will be devoted to discussing this relationship in more detail in view of its relevance to the present study.

1.7.1. Ionic (Unco-ordinated) Carboxylates

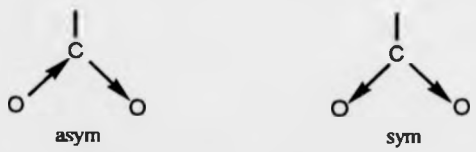
The carboxylates of highly electropositive elements such as sodium and potassium are reported to be ionic. The ionic nature of the formate group in sodium formate **(1.26)** has been shown by X-ray analysis.[118] The sodium has six oxygen neighbours at an average distance of 2.44Å which is exactly equal to the distance predicted on the basis of ionic radii .



(1.26)

The IR spectrum of these compounds shows a disappearance of the free acid carbonyl band at 1710cm^{-1}, and the occurrence of intense bands arising from the asymmetric and symmetric COO stretching modes. The separation between these bands, Δ, as defined below, and the variations in their positions have been very widely used in assigning structures and the carboxylate bonding mode from IR spectral data.[117,119]

For $M^+(O_2CR)^-$, Δ, is highly dependent on the nature of R.[120]



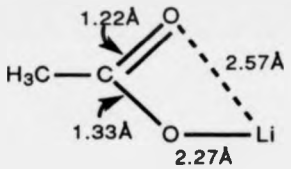
$$\Delta = \upsilon(COO)_{asym} - \upsilon(COO)_{sym}$$

For $Na(O_2CMe)$,[121] $\Delta = (1578 - 1414)\ cm^{-1} = 164cm^{-1}$

The variation of Δ with change in cation is quite small for acetates. This insensitivity to change is consistent with an ionic formulation. The symmetric structure of the ionic carboxylate group is also supported by close similarity of their vibrational spectra with those of nitro compounds. The assignments for CH_3NO_2 and CD_3NO_2 were used as an aid in assigning the frequencies in the spectra of $CH_3CO_2^-$ and $CD_3CO_2^-$.[122]

1.7.2. Unidentate Co-ordination

As a unidentate ligand, the carboxylate is expected to lose the equivalence of the two C-O bonds found in the anion and to have one M-O distance considerably shorter than the next shortest M-O contact as in $[Li(O_2CMe).2H_2O]$ shown **(1.28)**.[123]



(1.28)

If the C-O bond orders are appreciably affected, a pseudo ester configuration is obtained. The inequivalence of the two C-O bonds forms the basis of the IR method of detecting this form of co-ordination.[119] Unidentate carboxyl ligation is generally associated with an increase of the $\upsilon(COO)_{asym}$ band to a higher energy, and a decrease in the $\upsilon(COO)_{sym}$ band relative to the free ion, thus increasing the value of Δ. High values of Δ have found extensive use as indicators of unidentate carboxylate co-ordination and generally Δ is found to be greater than $200cm^{-1}$.[117]

However, some anomalies to this trend may occur. Interaction of the free oxygen atom with other entities in the molecule or with solvent molecules always remains a possibility. This serves to modify these distinctive structural features and Δ may be reduced. In nickel acetate tetrahydrate $\Delta=107cm^{-1}$, the small separation is due to

intramolecular H-bonding between an unco-ordinated carboxylate oxygen atom and a water molecule leading to equation of the two C-O bonds.[124] It may also be possible that with increasing the size of the metal, the compound can assume an unsymmetrical chelating structure by a weak interaction with the second oxygen atom, therefore lowering the value of Δ.

1.7.3. Bidentate Chelating Co-ordination

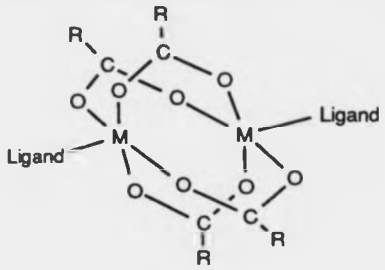
There are fewer examples of bidentate chelating co-ordination to give a four membered ring. This appears to be the least favoured mode of attachment and relief of the steric factors results in an extensive chemistry of appreciably unsymmetrical forms. With $[Sn(O_2CMe)_4]$,the metal is nearly eight co-ordinate.[106] However, there is not enough space round the metal for the eight oxygen atoms, and therefore one carboxylate is asymmetrical. From a symmetry viewpoint the C-O frequencies should not be expected to be different from those observed in the free ion spectrum. Although having a heavy atom attached to each oxygen may cause some shifting of these frequencies such changes are in practice rather small.[117,119]

The equivalence of the two C-O distances in both symmetrical chelation and bridging means that the technique of IR spectroscopy has a very limited use for differentiating between these two modes. Values of Δ significantly less than ionic values are found to be indicative of chelating and / or bridging carboxylates. Generally smaller values for chelating may be anticipated, but this should not form the sole basis of structural conclusions.

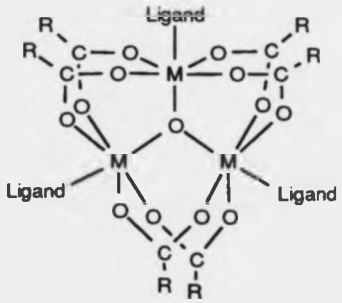
1.7.4. Bridging Co-ordination

The classical structure of *syn-syn* bridging is the most common co-ordination mode for the carboxylate ligand. Within this class , the two most widely studied systems

are the paddlewheel structure for binuclear complexes **(1.29)** and the triangular carboxylates for trimetal systems **(1.30)**.[111]



(1.29)



(1.30)

The other bridging modes are generally found in polymeric carboxylate complexes. Carboxylate bridging in the *anti-syn* or *anti-anti* configurations results in large metal-metal separations while *syn-syn* bridging may allow the 'close' approach of the two metal atoms leading to a variety of metal-metal interactions ranging from essentially no interaction, through weak spin pairing, to strong interactions.[125]

Usually the equivalence of the carbon-oxygen bonds is retained and recognition of the mode of co-ordination is best carried out by structural determination. A correlation of Δ with bridging or chelation of the ligand has been attempted for acetate systems, where a small Δ value ($<105 cm^{-1}$) may indicate chelation rather than bridging, but this is not a definitive method of distinction.[117]

In conclusion. three useful correlations between carboxylate stretching frequencies and the ligand co-ordination mode have been justified for acetate and also trifluoroacetate complexes in the major review by Deacon and Phillips.[117] Namely,

(a) Separations between υ(COO) frequencies (Δ) substantially greater than the ionic value are indicative of unidentate carboxylate ligation.

(b) Separations significantly less than the ionic values are indicative of the presence of chelating and / or bridging carboxylate groups.

(c) For acetates only, very low separations generally indicate chelation or a combination of chelation and bridging.

There appears to be no substantial reasons why the conclusions a-c should not also apply to co-ordination of other simple carboxylate ions RCO_2^- (R=alkyl or aryl), at least in general terms. However, it would be unwise to extrapolate these conclusions to more complex carboxylates such as amino acids or other carboxylates with donor atoms adjacent to the carbonyl function. Some carboxylate stretching frequencies of the acetate ligand for a range of different co-ordination modes are displayed in Table 1.8 .

Table 1.8 Carboxylate stretching frequencies (cm^{-1}) of metal acetates having differing co-ordination modes.

Bonding Mode	$\upsilon(COO)_{asym}$	$\upsilon(COO)_{sym}$	Δ	Ref.
Unidentate:				
$[Si(O_2CMe)_4]$	1760	1270	490	126
$[Sb(O_2CMe)_2Ph_3]$	1633	1320	313	127
Chelating				
$[Ru(O_2CMe)H(Ph_3P)_2]$	1526	1451	75	128
$[Zn(O_2CMe)_2.2H_2O]$	1550	1456	94	129
$[Mn(O_2CMe)(CO)_2(Ph_3P)_2]$	1520	1437	83	117
Bridging:				
$[Zn_4O(O_2CMe)_6]$	1600	1441	159	129
$[Be_4O(O_2CMe)_6]$	1639	1483	156	129
$[\{Rh(O_2CMe)_2(C_5H_5N)\}_2]$	1590	1430	160	117
Ionic:				
$[Na(O_2CMe)]$	1578	1414	164	121

In those cases where it is not possible to obtain a crystal structure the evidence obtained from IR spectroscopy offers an indication of the respective mode of co-ordination, given the proviso that such deductions have to be regarded as tentative, and need to be supplemented by other data before anything approaching a definitive statement can be made.

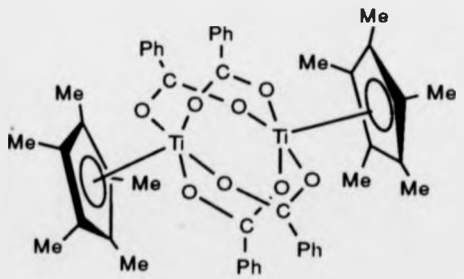
1.8. Titanium Cyclopentadienyl Carboxylate Compounds

Many cyclopentadienyl titanium carboxylate species have been structurally and spectroscopically characterised. Although only indirectly relevant to the present work, the important points in this vast area of titanium carboxylate chemistry will be highlighted in this section. Particularly, where possible, IR spectral data for these compounds will be discussed in relation to the detection of the carboxylate co-ordination modes.

1.8.1 Titanium(III) Cyclopentadienyl Carboxylate Species

A variety of monocyclopentadienyltitanium(III) carboxylates of the general formula $[CpTi(O_2CR)_2]$ have been prepared by Coutts *et al* (R=CF_3, Me, Et, ^nPr, Ph)[130] and Pasynskii (R=CF_3, Ph, *m*-FC_6H_4).[131] Although titanium(III) has a $3d^1$ configuration, the green-brown products are virtually diamagnetic. Analytical data suggested a dimeric structure with a superexchange interaction occurring between the titanium atoms through the π-system of the carboxylate bridges. Such a dimeric structure was confirmed by Tarkhova *et al* with the X-ray structure of $[\{CpTi(O_2CPh)_2\}_2]$ revealing a paddlewheel configuration with penta-co-ordinate titanium atoms.[132]

The analogous $[Cp^*Ti(O_2CPh)_2]$ **(1.31)** has been recently characterised.[133] The titanium atoms are separated by a distance of 3.660Å, thus eliminating the possibility of any metal-metal interaction. The geometry about each titanium atom is of the four-legged piano-stool type.



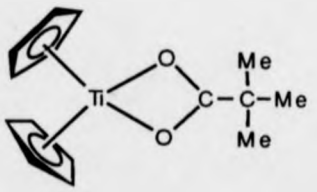
(1.31)

Selected IR data for compounds of this type are displayed in Table 1.9. The separation of the carboxylate bands, Δ, for these compounds is indicative of a bridging carboxylate mode as discussed previously.

Table 1.9 IR spectral information (cm^{-1}) for monocyclopentadienyltitanium(III) and dicyclopentadienyltitanium(III) carboxylates.

Compound	$\upsilon(COO)_{asym}$	$\upsilon(COO)_{sym}$	Δ	Ref.
$[CpTi(O_2CPh)_2]$	1566	1400	166	130
$[Cp^*Ti(O_2CPh)_2]$	1555	1385	170	133
$[CpTi(O_2CMe)_2]$	1595	1425	170	130
$[Cp^*Ti(O_2CMe)_2]$	1613	1430	183	133
$[Cp_2Ti(O_2CH)]$ **(a)**	1550	1435	115	134
$[Cp^*_2Ti(O_2CH)]$ **(b)**	1554	1378	176	135
$[Na(O_2CH)]$ **ionic**	1567	1366	201	118
$[Cp_2Ti(O_2CMe)]$	1525	1460	65	134
$[Cp_2Ti(O_2CPh)]$	1505	1425	80	134
(a), (b) see text below				

Dicyclopentadienyltitanium(III) carboxylates $[Cp_2Ti(O_2CR)]$ (R=H, Me, Ph, $CH_3(CH_2)_8$, $CH_3(CH_2)_{16}$) have been prepared by the reaction of the respective sodium carboxylates with $[Cp_2TiCl]$.[134] The blue-green products are monomeric and structure elucidation of $[Cp_2Ti(O_2CCMe_3)]$ shows a pseudo-tetrahedral structure containing a bidentate chelating trimethylacetate ligand with titanium η^5-bonded to the cyclopentadienyl rings **(1.32)**.[136]

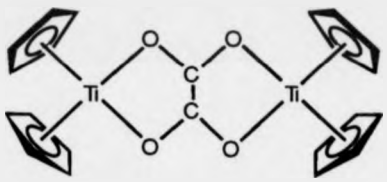


(1.32)

The bidentate chelating mode of the carboxylate ligand is additionally suggested by low Δ values in their IR spectra, as shown in Table 1.9.

For compound **(b)** $\Delta = 176 cm^{-1}$, which is greater than that of the Cp derivative **(a)**, $\Delta = 115 cm^{-1}$. The move to an increased Δ suggests an increase in the ionicity of the titanium carboxylate bond going from Cp to Cp*, an effect interpreted as a consequence of the inductive effects due to methyl substitution of the Cp rings.

Studies utilising dicarboxylic acids have also been carried out. Thus μ-oxalatobis[di-(η^5-cyclopentadienyl)titanium] has been structurally characterised **(1.33)** and found to be a binuclear species.[137] The oxalato group acts as a planar tetradentate bridging ligand with the titanium atoms displaced in a *cis* fashion out of the $(C_2O_4)^{2-}$ plane. In solution, the paramagnetic complex was rapidly decomposed by air.



(1.33)

Hendrickson and co-workers have synthesised a wide variety of binuclear dicyclopentadienyltitanium(III) dicarboxylates $[\{(\eta^5\text{-}C_5H_5)_2Ti\}_2(O_2CRCO_2)]$ (R=aliphatic, aromatic, cyclic aliphatic, unsaturated) in the study of magnetic exchange interactions but none of the products were structurally characterised.[138] The $(O_2CRCO_2)^{2-}$ anion also bridges in a bis-bidentate fashion forming four membered chelate rings.

1.8.2. Titanium(IV) Cyclopentadienyl Carboxylate Species

The tris-carboxylate derivatives of the general formula $[CpTi(O_2CR)_3]$ are normally prepared from the corresponding chlorides using the silver or potassium salt of the appropriate carboxylic acid.[139] A number of these monocyclopentadienyltitanium tris-carboxylates have been reported but their characterisation has been limited to

elemental analysis and IR spectroscopy. The yellow-orange solids are reasonably soluble in polar organic solvents and hydrolyse readily with elimination of the carboxylic acid.

The reaction between [Cp*TiMe$_3$] and carboxylic acids RCO_2H (R=Me, Ph, *p*-$MeOC_6H_4$) leads to cleavage of the Ti-Me bonds and subsequent carboxylate ligation.[133]

$$[Cp^*TiMe_3] + 3RCO_2H \longrightarrow [Cp^*Ti(O_2CR)_3] + 3CH_4$$
$$(R=Me, Ph, p\text{-}MeOC_6H_4)$$

If a lower molar ratio of acid:Ti is utilised, no bis or monosubstituted species may be isolated in a pure state, even at low temperatures.

Spectral investigation of these compounds indicates a small separation, Δ, between the carboxylate stretching modes in the IR, as shown in Table 1.10, intimating bidentate co-ordination of the carboxylate ligands.

Table 1.10 IR spectral data (cm^{-1}) for some [Cp*Ti(O_2CR)$_3$] species

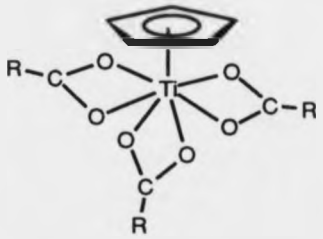
Compound	$\upsilon(COO)_{asym}$	$\upsilon(COO)_{sym}$	Δ	Ref.
[Cp*Ti(O_2CMe)$_3$]	1540	1430	110	133
[Cp*Ti(O_2CPh)$_3$]	1530	1420	110	133
[Cp*Ti($O_2CC_6H_4OMe$-*p*)$_3$]	-*	1430	<80*	133

* Due to overlap of the asymmetric stretching band with phenyl ring vibrations, Δ is assigned to a value no greater than 80cm^{-1}.

Confirmation of the carboxylate bonding mode has been achieved by structure elucidation of [Cp*Ti(O_2CPh)$_3$]. The compound was found to contain seven co-ordinate titanium in a distorted pentagonal bipyramidal environment (**1.34**).[133]

Dicyclopentadienyltitanium(IV) carboxylates, [$Cp_2Ti(O_2CR)_2$], are generally yellow-orange to red compounds with limited air, water and thermal stabilities, and have been extensively researched. Some of this work has been reviewed.[140] They are usually

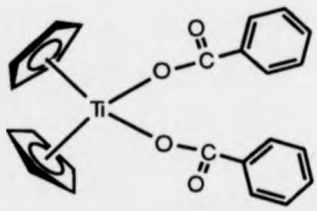
prepared by the reaction of $[Cp_2TiCl_2]$ with a silver (or alkali metal) carboxylate in THF under anaerobic conditions.



(1.34)

Early workers in this area proposed monodentate carboxylate co-ordination due to the occurrence of high carboxylate stretching frequencies in the IR spectra of these compounds and therefore a tetrahedral monomeric structure was proposed.

Structural investigation of $[Cp_2Ti(O_2CPh)_2]$ **(1.35)**[141] and $[Cp_2Ti(O_2CC_6H_4NO_2\text{-}p)_2]$[142] reveals a bent metallocene structure in which the titanium atom is attached to two monodentate benzoate ligands and two η^5-Cp groups.



(1.35)

The centroids of the Cp ligands and the co-ordinated atoms define a distorted tetrahedron, the η^5-rings being nearly staggered.

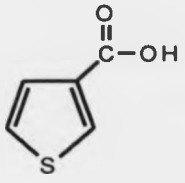
Some spectral information for these compounds indicating the large separation, Δ, of the carboxylate stretching frequencies is shown in Table 1.11. It is apparent from the Δ values obtained that there is some validity in the suggested correlation with the bonding mode of the carboxylate group, as discussed previously.

Dang *et al* synthesised thirty-two *o*-, *m*- and p-substituted benzoate complexes of the type $[Cp_2Ti(O_2CC_6H_4X)_2]$ and characterised them by ^1H and ^{13}C NMR and also IR spectroscopy.[147] With the latter method, Δ ranged from 300-370cm^{-1} for all the compounds studied. Similarly, $[Cp'_2Ti(O_2CC_6H_4X)_2]$ ($Cp'=\eta^5$-MeC_5H_4; X=*o*-, *m*-, *p*-halo, *o*-, m-, *p*-NO_2, *o*-, *m*-, *p*-Me) have been reported.[143] The *o*-methyl derivative has a bent metallocene structure similar to $[Cp_2Ti(O_2CPh)_2]$. The two Cp rings are eclipsed with the methyl substituents orientated in the same direction. For this large range of compounds, strong bands are observed in the 1650-1626cm^{-1} and 1345-1295cm^{-1} regions of the IR spectra giving a high Δ value of approximately 290cm^{-1}.

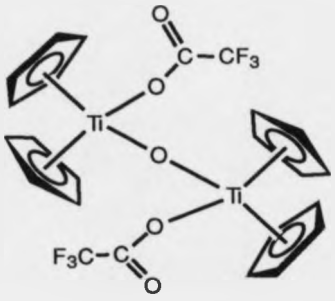
Table 1.11 IR data (cm^{-1}) for compounds of the type $[Cp_2Ti(O_2CR)_2]$

Compound	$\upsilon(COO)_{asym}$	$\upsilon(COO)_{sym}$	Δ	Ref.
$[Cp_2Ti(O_2CPh)_2]$	1642	1350	292	141
$[Cp_2Ti(O_2CC_6H_4Me\text{-}p)_2]$	1629	1338	291	143
$[Cp_2Ti(O_2CC_6H_4NH_2\text{-}o)_2]$	1620	1352	268	144
$[Cp_2Ti(O_2CCH{=}CPh).(PhC{\equiv}CCO_2H)]$	1680	a	a	144
$[Cp_2Ti(O_2CCF_3)_2]$	1710	a	a	146
$[Cp_2Ti(O_2CCH_2NHCOPh)_2]$	1655	1375	280	144
[a] unassigned				

Cyclopentadienyltitanium(IV)chloro carboxylate species have been less easy to prepare, with very few being reported. The reaction of thiophenecarboxylic acids, e.g. 3-thiophenecarboxylic acid **(1.36)**, with $[Cp_2TiCl_2]$ produced products of the type $[Cp_2TiCl(O_2CR)]$ and $[Cp_2Ti(O_2CR)_2]$.[148] From IR investigations Kapoor *et al* proposed a bidentate chelating mode for the carboxylate, the ring sulphur atom not participating with co-ordination to the metal centre.



(1.36)

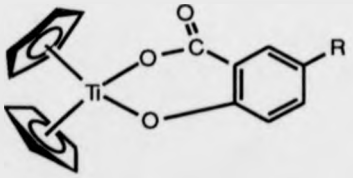


(1.37)

The reactions of $[Cp_2TiL_2]$ (L=α-thienyl) with the carboxylic acids RCO_2H [R=C_6F_5, CF_3, CCl_3, CBr_3, $C_6H_3(NO_2)_2$] give, in good yields, the products $[Cp_2Ti(O_2CR)_2]$.[149] Similar reactions of $[Cp_2TiCl(L)]$ with the acid or the sodium salt produces $[Cp_2TiCl(O_2CR)]$ derivatives, thereby retaining the Ti-Cl character of the molecule.[150]

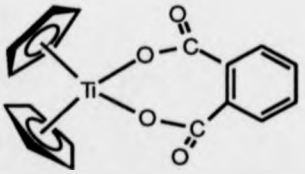
For $[Cp_2Ti(CR=CHR)(O_2CCF_3)]$ (i) the (R=H, Me) derivatives have been used as starting materials in the synthesis of titanocene trifluoroacetate compounds.[151] The complexes (i) react with trifluoroacetic acid to give the bis-carboxylate $[Cp_2Ti(O_2CCF_3)_2]$. The reaction of (i) with water gives the oxo bridged binuclear complex $[\{Cp_2Ti(O_2CCF_3)\}_2(\mu_2\text{-}O)]$ **(1.37)** which has been characterised by X-ray diffraction and found to contain monodentate carboxylate groups.

Di(η^5-Cp)salicylato **(1.38)** and di(η^5-Cp)phthalato **(1.39)** titanium(IV) complexes have been synthesised in aqueous solution using $[Cp_2TiCl_2]$.[152] No oxo-bridged species were formed due to a strict control of the reaction time.

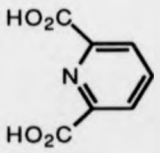


(R= H, CHO, NH_2)

(1.38)



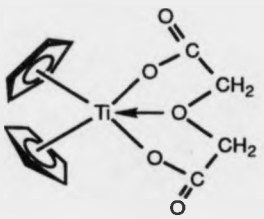
(1.39)



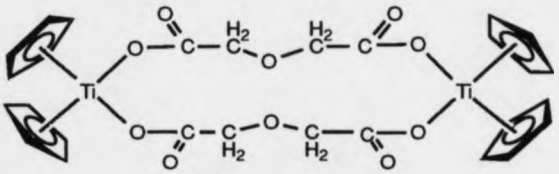
(1.40)

With 2,6-pyridine dicarboxylic acid **(1.40)** a similar reaction occurs to give $[Cp_2Ti(O_2CNC_5H_3CO_2)]$. This compound has also been prepared by Leik *et al* and structurally characterised by X-ray analysis showing monodentate carboxylate ligands and a co-ordinated ring nitrogen to produce a penta-co-ordinate environment around the metal centre.[153]

Further work by Thewalt concerning the reaction of $[Cp_2TiCl_2]$ with the disodium salt of oxydiacetic acid in the two phase system of H_2O / $CHCl_3$ has been successful in the preparation of a similar mononuclear carboxylate **(1.41)**.[154]



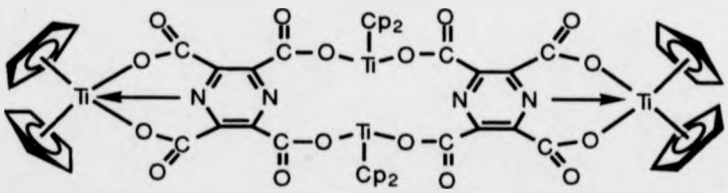
(1.41)



(1.42)

If CH_2Cl_2 is present in the latter reaction the dinuclear tetra-co-ordinate complex $[\{Cp_2Ti(O_2CCH_2OCH_2CO_2)\}_2] .2CH_2Cl_2$ **(1.42)** is produced where two dicarboxylate ligands bridge the titanium centres by monodentate co-ordination at either end of the acid chain. A similar binuclear species has been obtained from the reaction of $[Cp_2TiCl_2]$ with disodium fumarate, with subsequent X-ray structural characterisation.[155]

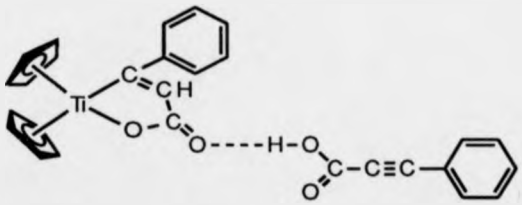
Reaction of $[Cp_2TiCl_2]$ with tetrasodium pyrazinetetra-carboxylate in the two phase system of H_2O / $CHCl_3$ gives the tetranuclear complex $[\{Cp_2Ti(C_8N_2O_8)TiCp_2\}_2]$ **(1.43)**.[156]



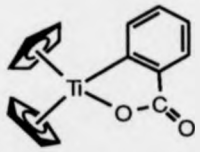
(1.43)

In this structure two of the titanium atoms are penta-co-ordinate and the other two are tetra-co-ordinate. An isostructural heterometallic complex $[\{Cp_2Ti(C_8N_2O_8)ZrCp_2\}_2]$ has been isolated with the zirconium atoms occupying the penta-co-ordinate positions and the titanium atoms occupying the tetra-co-ordinate positions. The reaction of **(1.43)** with aqueous HCl affords the penta-co-ordinate mononuclear complex $[Cp_2Ti(C_8H_2N_2O_8)]$.

$[Cp_2Ti(O_2CC{\equiv}CPh)_2]$ has been prepared from the reaction of $[Cp_2TiMe_2]$ and phenylpropiolic acid, and is an air-stable orange solid.[145] With the assistance of light the dark red titanium(IV) compound $[(\eta^5\text{-}Cp)_2Ti(PhC{=}CHCO_2).PhC{\equiv}CCO_2H]$ **(1.44)** is produced which has been crystallographically characterised. The molecule contains a monodentate carboxylate ligand with the titanium atom achieving tetra-co-ordination by σ-bonding to an unsaturated carbon to form a five membered ring. The complex is a 1:1 hydrogen bonded association with phenylpropiolic acid.



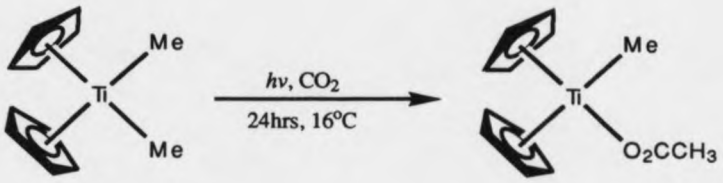
(1.44)



(1.45)

Insertion of carbon dioxide into a Ti-C bond has been found to occur when the gas is bubbled through a solution of $[Cp_2TiPh_2]$ in xylene at 80-90°C. The phenyl ring is then carboxylated and the metallocycle, $[Cp_2Ti(O_2CPh)]$ **(1.45)** forms.[157] The product is a diamagnetic, air stable, red compound with the titanium atom in a distorted tetrahedral environment.

The photolysis of $[Cp_2TiMe_2]$ in the presence of carbon dioxide has also resulted in CO_2 insertion into the transition metal-carbon bond producing $[Cp_2Ti(O_2CMe)Me]$ which was characterised by comparison with the equivalent compound synthesised from $[Cp_2TiMe_2]$ and acetic acid.[158]


Me
Ti
Me
hν, CO2
24hrs, 16°C
Me
Ti
O2CCH3

CHAPTER TWO

ROOM TEMPERATURE REACTIONS OF $TiCl_4$ WITH THE ALKYL ACIDS RCO_2H (R=Me, Et, CMe_3)

2. INTRODUCTION
Non-Cyclopentadienyl containing Titanium Carboxylates

The previous chapter has introduced just some of the cyclopentadienyl containing titanium carboxylates which have been reported to date. Continuing on the theme of titanium carboxylate species we now introduce some non-cyclopentadienyl containing species which are relevant to the work carried out in this thesis. However, few structural characterisations exist and therefore the bonding mode of the carboxylate may not be unequivocally established. IR spectroscopy can therefore be a useful aid in establishing the bonding mode of the carboxylate ligand. These latter observations will be discussed.

2.1. Titanium(II) Carboxylates

Titanium(II) carboxylates have not been widely researched, most probably due to their extreme air sensitivity and the difficulties in their preparation. $[Ti(O_2CCF_3)X.Et_2O]$ (X=Cl, Br) have been synthesised from the interaction of $[Ti(O_2CCF_3)_2]$ and SOX_2 in diethyl ether. The monoetherate adducts have been found to be catalytically active in the stereospecific polymerisation of butadiene.[159]

2.2. Titanium(III) Carboxylates

The yellow-brown solids $[Ti(O_2CMe)Cl_2]$ and $[Ti(O_2CMe)_2Cl]$ have been prepared from the action of acetic anhydride on $TiCl_3$. When a mixture of acetic acid with acetic anhydride is used, the acid adduct $[Ti(O_2CMe)Cl_2.MeCO_2H]$ is produced.[160] Although elemental analysis allowed products of reasonable stoichiometry to be proposed the authors note that these may have been the result of fortuitous sampling and that the substituted acetate products may not be pure. All three compounds are non-crystalline, involatile and insoluble in organic solvents. Their IR spectra were very similar and showed bands at 1530, 1400 and 290cm^{-1} which were assigned to $\upsilon(COO)_{asym}$, $\upsilon(COO)_{sym}$ and υ(Ti-Cl) respectively, giving a Δ value of 130cm^{-1} thus implying the

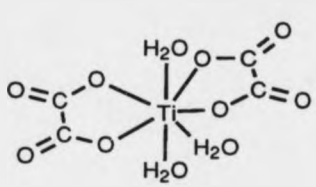
presence of symmetrical bridging carboxylate groups. The same workers were unable to synthesise the trisubstituted product [$Ti(O_2CMe)_3$]. However, the trisubstituted [$Ti(O_2CMe)_3$] has been reportedly prepared from the reduction of $TiCl_4$ with granulated zinc followed by the addition of sodium acetate,[161] and a dark green titanium(III) formate [$Ti(O_2CH)_3$] has been prepared by reaction of formic acid with basic titanium carbonate.[162]

A route to [$Ti(O_2CCF_3)_3$] is from the reaction of tetramethyltitanium(IV) with trifluoroacetic acid at -50°C, which leads to a complete reduction of the titanium to produce the green, air and moisture sensitive product, which has a magnetic moment of 1.62.[163] Definitive structural information on this compound would be interesting since the IR spectrum of this compound gives strong evidence in support of unidentate trifluoroacetate bonding with $\upsilon(COO)_{asym}$ at 1675cm^{-1} and $\upsilon(COO)_{sym}$ at 1210cm^{-1} with Δ therefore having a value of 465cm^{-1} (compared with the ionic [$K(O_2CCF_3)$] where Δ=241cm^{-1}).[164] In spite of this evidence it seems unlikely that the metal centre is three co-ordinate , and a polymeric system appears more probable.

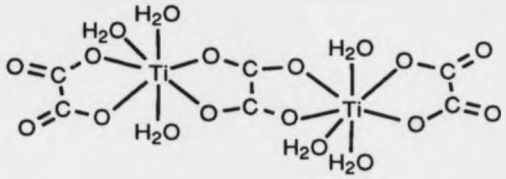
It is interesting to note that when an excess of acetic acid is added dropwise to a solution of tetrabenzyltitanium in *n*-pentane, a mixed valence green crystalline Ti(III,IV) species, formulated as [$\{Ti(O_2CMe)_3\}_4.\{Ti(O_2CMe)_4\}$] is precipitated.[163] The product was not considered to be a mixture of discrete Ti(III) and Ti(IV) acetates as many separation attempts were unsuccessful. The IR spectrum of this crystalline compound indicates the presence of both unidentate and bidentate co-ordination of the acetate ligands.

The titanium(III) oxalate salts [$K\{Ti(C_2O_4)_2\}.2H_2O$] and [$NH_4\{Ti(C_2O_4)_2\}.2H_2O$] have been isolated and can be readily dehydrated without oxidation of the titanium(III) centre to titanium(IV).[165] Spectral measurements indicate that no water is co-ordinated to the metal and it was proposed that the titanium atoms were linked by shared oxalate groups to give a polymeric structure. In contrast, the salt

$[Cs\{Ti(C_2O_4)_2(H_2O)_3\}.2H_2O]$ **(2.1)** has been fully characterised by X-ray diffraction and found to contain co-ordinated water molecules.[166]



(2.1)



(2.2)

The seven co-ordinate titanium is in a pentagonal bipyramidal environment with the oxalate anions situated equatorially along with one water molecule. The remaining two bonded water molecules are axially positioned.

A similar arrangement around the titanium metal centre occurs in the binuclear titanium(III) oxalate species $[\{Ti_2(C_2O_4)_3(H_2O)_6\}.4H_2O]$ **(2.2)** which has also been fully characterised.[167] As with $[Cs\{Ti(C_2O_4)_2(H_2O)_3\}.2H_2O]$ above, the titanium atoms have pentagonal bipyramidal geometry except here, both bridging and chelating carboxylate ligands are found.

2.3. Titanium(IV) Carboxylates
The Reaction of $TiCl_4$ with Carboxylic Acids

The reactions of $TiCl_4$ with carboxylic acids has been investigated by many research groups over the past thirty years, but so far, the structural characterisation of the resultant compounds has been limited. Ideally, the addition of stoichiometric amounts of acid to the reaction system should allow all four substituted titanium compounds to be prepared by the successive replacement of chlorine atoms by carboxylate ligands. This conjecture is shown in the equation below.

$$TiCl_4 + xRCO_2H \xrightarrow{\text{solvent}} [TiCl_{4-x}(O_2CR)_x] + xHCl$$

(R=alkyl, aryl ; x=1, 2, 3, 4)

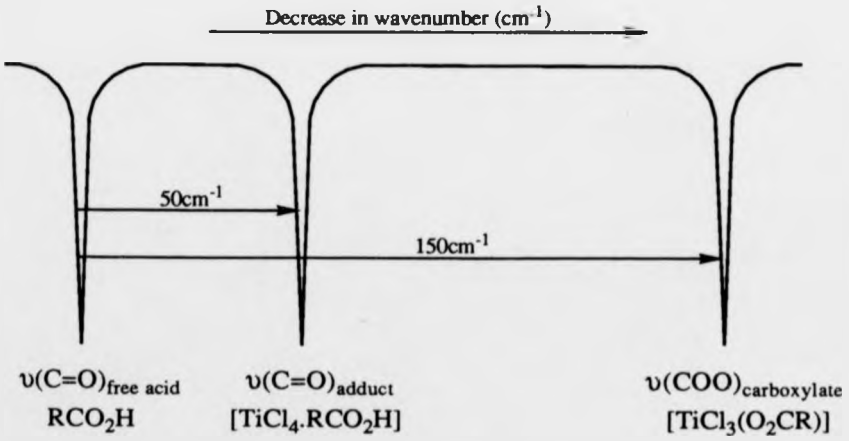
From this equation we can see that the monosubstituted derivative, $[TiCl_3(O_2CR)]$, is the first product arising from the elimination of one mole of hydrogen

chloride from the system. However, a much simpler case may be envisaged whereby on initial mixing of $TiCl_4$ with a carboxylic acid, an adduct of the type $[TiCl_4.RCO_2H]$ (R=alkyl or aryl) is produced. Addition compounds of the stoichiometry $[TiCl_4.L]$ generally have a dimeric structure through bridging chlorine atoms, with both of the titanium atoms in octahedral environments, as discussed in Chapter 1.

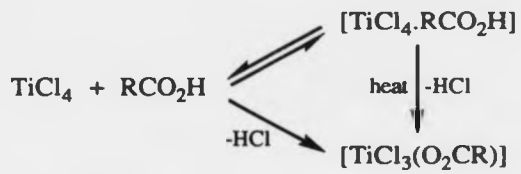
2.3.1. Acid Adducts and Monosubstituted Titanium Carboxylate species

The complexes $[TiCl_4.RCO_2H]$ (R=Ph, *p*-MeC_6H_4, 2,4,6-$Me_3C_6H_2$ and PhCH=CH) have been reportedly prepared by mixing $TiCl_4$ and the carboxylic acid in carbon tetrachloride.[168] It was proposed, from IR evidence that the acids were co-ordinated to the titanium through the carbonyl oxygen due to a lowering of the carbonyl stretching frequency from that of the free acid.

Mach and Drahorádová investigated the products of the reaction of $TiCl_4$ with carboxylic acids in benzene at room temperature, and the decrease in concentration of the carboxylic acid was followed quantitatively by IR spectroscopy.[169] The products of the 1:1 mole interaction of the Lewis acid with the acids were, in all cases, characterised by the decrease in intensity of the original acid carbonyl band and the concomitant growth of two new bands at lower wavenumbers as shown below.



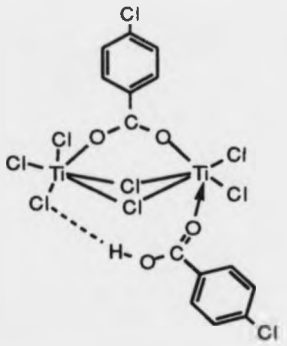
It was found that the intensity of $\upsilon(C{=}O)_{adduct}$ decreased on heating the reaction solution, while the intensity of $\upsilon(COO)_{carboxylate}$ increased. These interactions may be characterised by the following scheme.



Another feature of these interactions was the dependence of the product composition on the acid strength; the stronger acids gave more carboxylate, while the weaker acids gave more adduct.

An analogous adduct [$TiCl_4.Me_3CCOSH$] was prepared by the action of excess $TiCl_4$ on thiopivalic acid in dichloromethane at room temperature.[170] An IR study of the dark yellow solid showed a band at 2520cm^{-1} which could be attributed to the presence of an S-H band. In addition, a strong band at 1555cm^{-1} was assigned to a carbonyl absorption with a shift from the corresponding band of the free acid (1700cm^{-1}), thus indicating that the carbonyl oxygen is acting as a donor to the metal atom.

Earlier investigations in these laboratories on the $TiCl_4$-carboxylic acid systems has failed to identify the 1:1 adducts [$TiCl_4.RCO_2H$] as described above, but instead, a further type of co-ordinated acid product has been established. On reacting $TiCl_4$ and RCO_2H (R=*p*-ClC_6H_4, *p*-BrC_6H_4, *p*-FC_6H_4, CH=CHMe) at 0-25°C in a 1:1 molar ratio the bimetallic, air-sensitive yellow crystalline products of the formulation [$Ti_2Cl_7(O_2CR)(RCO_2H)$] are obtained.[170] X-ray structure determination of the *p*-chlorobenzoate **(2.3)** and crotonate derivatives revealed a binuclear species with an unusual feature of having both a carboxylate group and a carboxylic acid co-ordinated to the same metal centre. The two titanium atoms are in a distorted octahedral environment and are linked by two chlorine bridges and one carboxylate group. The acid group for both structures is orientated to give a close contact between the acid -OH and adjacent Cl.



(2.3)

In the case of the structurally analogous crotonate derivative $[Ti_2Cl_7(O_2CCH{=}CHMe)(CHMe{=}CHCO_2H)]$ the yield is very low (15%), with the major product being the monocarboxylate $[TiCl_3(O_2CCH{=}CHMe)]$. With the *para*-substituted benzoates the bimetallic intermediate is the only isolable product ,with no simple carboxylate being detected. The IR spectra of these latter compounds show similarities in the carboxylate region as shown in Table 2.1.

Table 2.1 IR spectral data (cm^{-1}) for the binuclear titanium carboxylate species $[Ti_2Cl_7(O_2CR)(RCO_2H)]$.

Compound	$\upsilon(C{=}O)_{free\ acid}$	$\upsilon(C{=}O)_{co\text{-}ord.acid}$	$\upsilon(COO)_{asym}$	$\upsilon(COO)_{sym}$	Δ
R=*p*-FC_6H_4	1690	1560	a	1410	a
R=*p*-ClC_6H_4	1680	1550	a	1400	a
R=*p*-BrC_6H_4	1680	1560	1580	1400	180
[a] unassigned due to the complexity of the 1600-1500cm^{-1} region					

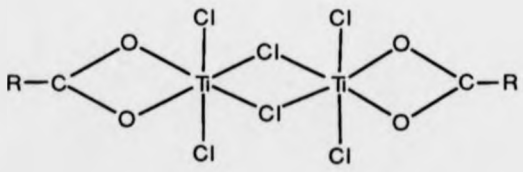
The presence of the carboxylic acid proton in these derivatives can be established from their 400MHz ^1H NMR spectra, and appears as a broad resonance at δ9-10.

As these compounds contain both co-ordinated acid and chlorine ligands at room temperature, it should, in theory, be possible to eliminate HCl with warming. Thus when $[Ti_2Cl_7(O_2CC_6H_4Cl\text{-}p)(p\text{-}ClC_6H_4CO_2H)]$ is dissolved in toluene and heated to 55°C for

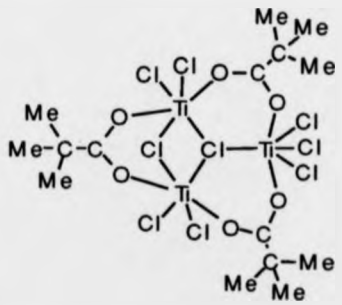
2 hr, the orange solid produced is formulated as $[TiCl_3(O_2CC_6H_4Cl\text{-}p)]$ which is in line with the reaction scheme shown below.

$$2TiCl_4 + 2RCO_2H \xrightarrow[0\text{-}25^oC]{\text{-HCl}} [Ti_2Cl_7(O_2CR)(RCO_2H)] \xrightarrow[55^oC]{\text{-HCl}} 2[TiCl_3(O_2CR)]$$

This also agrees with the direct preparation of the monocarboxylate species at slightly elevated temperatures. Thus the treatment of $TiCl_4$ (1.1 mol) with a carboxylic acid (1 mol) at room temperature followed by heating to 50-100°C yields the air-sensitive derivatives $[TiCl_3(O_2CR)]$ (R=Ph, *o*-MeC_6H_4, *p*-MeC_6H_4, 2,4,6-$Me_3C_6H_2$, $CMePh_2$, $CHMe_2$, CMe_3, C_9H_6N, CH=CHPh or CH=CHMe).[170,171] Although a slight excess of $TiCl_4$ is desirable it was found that when used to a larger excess the $TiCl_4$ was retained tenaciously by the products, even after successive washing with solvent and / or pumping under vacuum. Compounds of the type $[TiCl_3(O_2CR)]$ (R=alkyl, aryl) have been prepared previously by Amaudrut *et al* (R=CH_2Cl, $CHCl_2$, CCl_3, CMe_3, ^nBu, ^iBu)[172] (R=Me)[173] and Kapoor and co-workers (R=Me, Et, ^nPr, ^nBu, ^nPentyl)[174] but their characterisation was limited to elemental analysis, IR spectroscopy, and ebullioscopic measurements. In these earlier studies the monocarboxylate was proposed to be dimeric with the hexa-co-ordinate titanium atoms bridged by two chlorine atoms, and with one carboxylate ion bidentate chelating to each titanium **(2.4)**.[173]



(2.4)

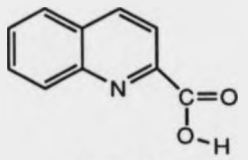


(2.5)

The structure of the trimethylacetate derivative $[TiCl_3(O_2CCMe_3)]$ **(2.5)** was determined by X-ray analysis and the compound was found to be trimeric in the solid

state.[170] Each titanium atom is in a distorted octahedral environment and in a triangular framework, linked by both bridging carboxylate and chlorine ligands.

The product with quinoline-2-carboxylic acid **(2.6)** shows analytical and spectral data indicative of $[TiCl_3(O_2CC_9H_6N)]$ but is less soluble than the other derivatives, possibly due to association arising from N-Ti interactions.[170]



(2.6)

Some pertinent IR spectral data for these compounds are given in Table 2.2 .

Table 2.2 Carboxylate stretching frequencies (cm^{-1}) of some titanium(IV) monocarboxylate species

Compound	$\upsilon(COO)_{asym}$	$\upsilon(COO)_{sym}$	Δ	Ref.
$[TiCl_3(O_2CMe)]$	1640	a	a	174
	1595	1430	165	
$[TiCl_3(O_2CEt)]$	1620	a	a	174
	1580	1420	160	
$[TiCl_3(O_2CPh)]$	1555	1410	145	170
$[TiCl_3(O_2CC_6H_4Me\text{-}p)]$	1530	1410	120	170
$[TiCl_3(O_2CCMe_3)]$	1643	1508	135	170
	1553	1428	125	
[a] unassigned				

The values for Δ in Table 2.2 (120-165cm^{-1}) are indicative of a bridging bonding mode for the carboxylate ligand. For some of the compounds, especially the trimethylacetate ($R=CMe_3$) derivative, two distinct sets of asymmetric and symmetric absorption bands are observed. This is confirmed by the crystal structure of

$[TiCl_3(O_2CCMe_3)]$ **(2.5)** which shows the presence of different symmetry related bridging carboxylate groups within the molecule.

2.3.2. Bis-Carboxylate species of the type $[TiCl_2(O_2CR)_2]$

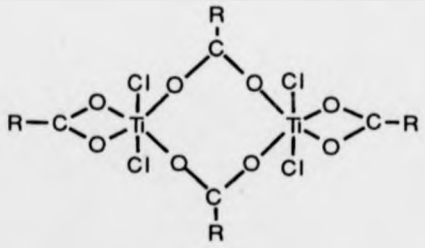
Titanium bis-chlorocarboxylates of the formula $[TiCl_2(O_2CR)_2]$ have also been reported in earlier studies, and were prepared by the addition of $TiCl_4$ to the carboxylic acid in a 1:2 mole ratio.[172,174,175]

$$TiCl_4 + 2RCO_2H \xrightarrow[25°C]{\text{solvent}} [TiCl_2(O_2CR)_2] + 2HCl$$

(R=alkyl, aryl)

Preparative temperatures for this type of compound are somewhat lower than those of the monocarboxylates, being at room temperature or below. The bis-carboxylates are extremely sensitive to moisture, fuming in moist air, with their colour changing from yellow to white, probably due to hydrolysis.

A large amount of work has been carried out concerning the reactions of titanium(IV) chloride with carboxylic acids by Amaudrut and co-workers. Compounds of the type $[TiCl_2(O_2CR)_2]$ (R=Me, Et, CMe_3, CH_2Cl, $CHCl_2$) were characterised from their X-ray powder diffraction data and IR studies.[175] Three absorption bands between 1700 and 1300cm^{-1} were assigned to carbon-oxygen bond stretching vibrations and the presence of two types of carboxylate ligands were suggested, one having bidentate chelating groups, and the other with symmetrical bridging groups between two titanium atoms. From this information, a structure **(2.7)** was proposed for the $[TiCl_2(O_2CR)_2]$ compounds.



(2.7)

Of the three absorption bands, it was proposed that the central carboxylate band, in the region 1550-1520cm^{-1}, was due to the overlapping of an asymmetric and a symmetric carboxylate stretching mode. Based on this factor, the predicted Δ values may be calculated from the results, as shown in Table 2.3.

Table 2.3 Carboxylate stretching frequencies (cm^{-1}) of $[TiCl_2(O_2CR)_2]$ species

Compound	$\upsilon(COO)_{asym}{}^a$	$\upsilon(COO)_{sym}{}^a/_{asym}{}^b$	$\upsilon(COO)_{sym}{}^b$	Δ^a	Δ^b	Ref.
$[TiCl_2(O_2CMe)_2]$	1655	1550	1430	115	120	175
$[TiCl_2(O_2CEt)_2]$ *	1655	1525	1405	130	120	175
$[TiCl_2(O_2CEt)_2]$ *	1600	1520	1400	80	120	175
$[TiCl_2(O_2CCMe_3)_2]$	1655	1520	1420	135	100	175

* Two forms were prepared for the propanoate derivative
$\Delta^a=\upsilon(COO)_{asym}{}^a-\upsilon(COO)_{sym}{}^a$
$\Delta^b=\upsilon(COO)_{asym}{}^b-\upsilon(COO)_{sym}{}^b$

In accord with these spectral measurements, Kapoor and co-workers have prepared a similar series of compounds, and also reported the occurrence of three bands in the carboxylate region of the IR spectrum.[174] The vibrational bands are situated at similar frequencies to the compounds investigated by Amaudrut *et al*.

Analogous dibromo-bis-carboxylate species of the formula $[TiBr_2(O_2CR)_2]$ (R=Me, Et, CMe_3, CH_2Cl, CH_2F, $CHCl_2$) have been synthesised and compared with the chloride derivatives.[176] The yellow, hygroscopic solids were characterised by Debye-Scherer spectra and IR measurements. Three characteristic bands occurred in the carboxylate region at 1650, 1540 and 1400cm^{-1}, implying the presence of two types of carboxylate groups as previously discussed. The dimeric model **(2.7)** was again proposed.

In contrast to the aforementioned structure, Schwartz *et al* suggested an all bridging binuclear species **(2.8)** based on IR spectral measurements and molecular weight determinations carried out for the acetate and propanoate derivatives.[177]

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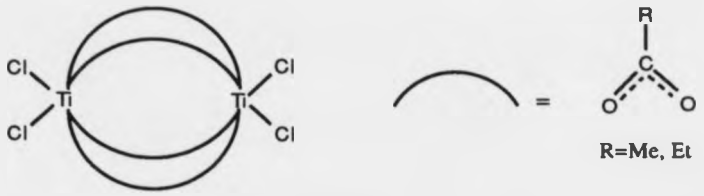


(2.8)

The bis-formate $[TiCl_2(O_2CH)_2]$ has been prepared from $TiCl_4$ and formic acid at a temperature of -10°C in dichloromethane.[178] The compound is extremely hygroscopic, reacting with water to give an oxo titanium(IV) carboxylate as shown by the equation below.

$$[TiCl_2(O_2CH)_2] + H_2O \longrightarrow [TiO(O_2CH)_2] + 2HCl$$

A communication by Uh *et al* reports the preparation of $[TiCl_2(O_2CR)_2]$ (R=Me, Et, MeCH=CH, Ph, *o*-HOC_6H_4) species in dichloromethane solvent,[179] but research in our own laboratories casts doubt on the claim where R=Ph, since detailed research has shown that the bis-carboxylate could not be isolated, even on increasing the reaction temperature.

Although a number of bis-carboxylates have been synthesised, no structural analyses have been carried out to verify or dispute the proposals put forward concerning the stoichiometry and arrangement of ligands around the titanium centre. Clearly, this area of titanium(IV) carboxylate chemistry is still ill-defined and in need of further clarification. The many claims and apparent confusion in this area has prompted some of the work undertaken in this present study as will be discussed later in this chapter.

2.3.3. Tris-Carboxylate Compounds of the type $[TiCl(O_2CR)_3]$

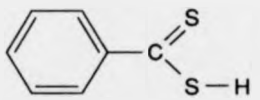
The tris-carboxylates $[TiCl(O_2CR)_3]$ (R=H, Et, *o*-HOC_6H_4, $PhCH_2$) have been reported by Jaura and co-workers from the action of the respective carboxylic acid on $TiCl_4$,[180] but many papers have reported that the substitution of chlorine for carboxylate

ligands does not proceed after the bis-carboxylate derivative $[TiCl_2(O_2CR)_2]$ for (R=aryl, alkyl).

It was postulated by Mehrotra *et al* from the reaction of $TiCl_4$ with benzoic acid that $[TiCl_3(O_2CPh)]$ and $[TiCl_2(O_2CPh)_2]$ were prepared both directly and rapidly and that the 1:3 reaction goes slowly after the bis-carboxylate is formed.[181] It was proposed that the tris-carboxylate $[TiCl(O_2CPh)_3]$ was formed during the reaction, but being unstable, undergoes decomposition which is accelerated by heat according to the scheme below.

$$[TiCl(O_2CPh)_3] \longrightarrow [TiO(O_2CPh)_2] + PhCOCl$$

Kapoor and co-workers found a similar dilemma. Reaction of excess acid with $TiCl_4$ produced only $[TiO(O_2CR)_2]$ (R=Me, Et, ^{n}Pr, ^{n}Bu, ^{n}Pentyl) derivatives.[174] However, refluxing a mixture of $TiCl_4$ and acetic anhydride produced a coffee-brown powder which analysed as $[TiCl(O_2CMe)_3]$.



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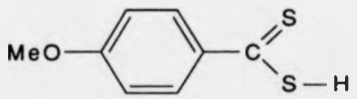


(2.10)

The preparation and characterisation of complexes formed from dithiobenzoic acid **(2.9)** and *p*-methoxydithiobenzoic acid **(2.10)** with $[TiCl_4.2N{\equiv}CEt]$ has been carried out to give apparently seven co-ordinate species of the type $[TiCl(S_2CR)_3]$ which were characterised by their IR spectra and elemental analyses.[182] These monochlorotitanium(IV) complexes are very susceptible to hydrolysis, especially in solution with the elimination of HCl, to give oxo species of the type $[\{Ti(S_2CR)_3\}_2O]$ which are also considered as seven co-ordinate.

2.3.4. Tetra-Carboxylate species of the type $[Ti(O_2CR)_4]$

Some claims have been made for the preparation of tetra-carboxylates of the type $[Ti(O_2CR)_4]$. Solvolytic reactions of $TiCl_4$ in the carboxylic acids CH_2ClCO_2H,[183]

$CHCl_2CO_2H$[184] and CCl_3CO_2H,[185] with heating, have given the corresponding tetra-carboxylate derivatives which have been characterised by elemental analysis and IR spectroscopy. IR spectral investigation of $[Ti(O_2CCHCl_2)_4]$ shows that there are no bands in the region of the metal-chlorine stretching modes. The dichloroacetate groups were proposed to be acting in both a bidentate chelating and bridging fashion. The tetra-carboxylates were proposed to be polymeric in nature.

$[Ti(O_2CMe)_4]$ and $[Ti(O_2CCH_2Cl)_4]$ have been reported from the reaction of $TiMe_4$ with the respective acid at low temperatures, the monochloroacetate derivative apparently containing traces of some titanium(III) reduction product. IR analysis of these two compounds indicated the presence of two different bonding modes; unidentate and bidentate, as shown in Table 2.4.[166]

Table 2.4 IR spectral data (cm^{-1}) for $[Ti(O_2CCH_2Cl)_4]$ and $[Ti(O_2CMe)_4]$.[166]

Compound	$\upsilon(COO)_{asym}$	$\upsilon(COO)_{sym}$	Δ
$[Ti(O_2CCH_2Cl)_4]$	1730	1300	430
	1570	1420	150
$[Ti(O_2CMe)_4]$	1725	1300	425
	1565	1435	130

For the tetra-acetate derivative $\Delta=430cm^{-1}$ which is much larger than the corresponding value for the ionic compound $[Na(O_2CMe)]$ ($\Delta=164cm^{-1}$)[121] therefore showing the highly unsymmetrical nature of some of the carboxylate groups present in the compound. The other set of asymmetric and symmetric stretching frequencies are in line with bidentate co-ordination of the ligand, but due to the apparent polymeric nature of these derivatives a bridging carboxylate mode may be tentatively assigned. These assumptions may also be applied to the monochloroacetate derivative.

In comparison to the reports of $[Ti(O_2CR)_4]$ species the titanium(IV) tetra-acetate derivative $[Ti(O_2CMe)_4.\ 2MeCO_2H]$ has been prepared by Gayer *et al*[186] and

Waddington and co-workers[187] from the reaction of $TiCl_4$ with potassium acetate and an acetic acid / acetic anhydride mixture in diethyl ether. However, titanium tetra-benzoate [$Ti(O_2CPh)_4$] has been reportedly prepared by the action of benzoic acid on $TiCl_4$ and it was proposed that the larger carboxylate groups do not allow the co-ordination of further ligands.[186]

2.4. RESULTS AND DISCUSSION

Full experimental details are presented in Chapter 8 on page 225.

As can be seen from the introduction to this section, structural evidence from X-ray diffraction studies for titanium chlorocarboxylate species is sparse in comparison to that of the cyclopentadienyl derivatives, which were discussed in Chapter 1. This is illustrative of the greater emphasis given to the organometallic derivatives of the Group IV elements over the past few decades in comparison to the development of new types of compounds, especially those not containing the Cp type of group. Another feature worthy of mention is the greater resistance of the Cp compounds including the titanium carboxylates to moisture, and therefore such species will be less liable to produce contaminant hydrolysis products during work-up and crystallisation procedures.

Indeed, structure elucidation of the intermediates $[Ti_2Cl_7(O_2CR)(RCO_2H)]$ (R=*p*-ClC_6H_4, MeCH=CH) and the monocarboxylate $[TiCl_3(O_2CCMe_3)]$ were only reported in 1991 and this work has opened up a renewed interest in these systems. Could it be possible that such species are also produced in the reaction of $TiCl_4$ with sterically hindered, or even, much stronger carboxylic acids? If not, then it would be interesting to isolate and characterise any new carboxylate species that are produced. With this information, it may be possible to discover if a relationship exists between the steric hindrance of the alkyl or aryl substituent of the acid, the stoichiometry of the reaction, and the arrangement of ligands around the titanium metal centre. Likewise acid strength may be a similar factor in determining the amount of substitution that occurs on reaction of the carboxylic acid with $TiCl_4$.

Continuing with the binuclear intermediate species which have been isolated $[Ti_2Cl_7(O_2CR)(RCO_2H)]$ (R=*p*-XC_6H_4; X=F, Cl, Br and R=MeCH=CH),[170,188] it was considered of interest to study the analogous reaction of $TiCl_4$ with lower alkyl chain carboxylic acids; namely acetic, propanoic and trimethylacetic acids. It is known that the monocarboxylate species $[TiCl_3(O_2CR)]$ (R=Me, Et, CMe_3) may be formed by the

action of $TiCl_4$ on the corresponding acid in a suitable solvent at temperatures in excess of 50°C. For this thesis, analogous reactions at room temperature have been investigated. The products $[Ti_2Cl_7(O_2CR)(RCO_2H)]$ (R=Et, CMe_3) have been isolated and are now reported.

2.4.1. Preparation of the species $[Ti_2Cl_7(O_2CR)(RCO_2H)]$ (R=Et, CMe_3)

The dropwise addition of $TiCl_4$ (1 mol) to a solution of RCO_2H (R=Et, CMe_3) (1 mol) in petroleum ether (b.p. 60-80°C) at ambient temperature, produces a clear yellow solution. After stirring for 1-2 hours, a yellow air-sensitive microcrystalline material begins to deposit which may be isolated for both acids in 80-90% yield. Analytical data is consistent with the products being of the formulation $[Ti_2Cl_7(O_2CEt)(EtCO_2H)]$ and $[Ti_2Cl_7(O_2CCMe_3)(Me_3CCO_2H)]$. The reaction may be shown by the equation below.

$$2TiCl_4 + 2RCO_2H \longrightarrow [Ti_2Cl_7(O_2CR)(RCO_2H)] + HCl$$
$$(R=Et, CMe_3)$$

The title compounds were further characterised by IR and ^1H NMR spectra as discussed below.

IR Spectra of the compounds $[Ti_2Cl_7(O_2CR)(RCO_2H)]$ (R=Et, CMe_3)

The most striking feature of the IR spectra of these compounds is the sharp, weak intensity band situated at 3276 (R=Et) and 3285cm^{-1} (R=CMe_3). This may be attributed to the [υ(OH)] of the co-ordinating carboxylic acid hydroxyl group. It has been noted previously, by Malhotra and Sud, that on adduct formation between monochloroacetic acid and Lewis acids such as $TiCl_4$, the absorption band due to the OH becomes very sharp.[189] The stretching frequency for the hydroxyl group appeared at the same position as has been reported for the hydroxyl group of the monomeric acid. They concluded that during adduct formation with strong Lewis acids, the intermolecular hydrogen bonded

structure of the associated carboxylic acid was broken, with subsequent strengthening of the O-H bond.

As was discussed previously in the introduction to this chapter, X-ray diffraction studies have shown for R=*p*-ClC_6H_4 **(2.3)** and MeCH=CH that the two titanium atoms are linked by both carboxylate and chlorine bridges, the remaining terminal sites being occupied by the co-ordinated acid and chlorine atoms.[170] For the $[Ti_2Cl_7(O_2CR)(RCO_2H)]$ derivatives with the *para*-substituted benzoic acids, the co-ordinated acid carbonyl stretching frequencies were assigned to bands at 1560 (R=*p*-FC_6H_4, *p*-BrC_6H_4) and 1550cm^{-1} (R=*p*-ClC_6H_4) as shown in Table 2.1. For the propanoate and trimethylacetate derivatives prepared in this work, the corresponding band was situated at 1601 (R=Et) and 1603cm^{-1} (R=CMe_3). The drop in frequency of the carbonyl stretching band on co-ordination compared to the free acid is 117 (R=Et) and 101cm^{-1} (R=CMe_3), slightly less than that in the analogous *p*-FC_6H_4 and *p*-ClC_6H_4 (130cm^{-1}) and the *p*-BrC_6H_4 (120cm^{-1}) species.

The asymmetric and symmetric carboxylate stretching frequencies of the bridging moiety are shown in Table 2.5 along with other relevant IR spectral data. The value of Δ, which is the separation between $\upsilon(COO)_{asym}$ and $\upsilon(COO)_{sym}$, may be calculated and is comparable with previous observations for bridging carboxylates in titanium systems.

Table 2.5 Some pertinent IR data (cm^{-1}) for the compounds $[Ti_2Cl_7(O_2CR)(RCO_2H)]$ (R=Et, CMe_3)

R	υ(OH)	υ(C=O) co-ord.acid	$\upsilon(COO)_{asym}$	$\upsilon(COO)_{sym}$	Δ	υ(Ti-Cl) terminal	υ(Ti-Cl) bridging
Et	3276	1601	1496	1365	131	432,415,369	273
CMe_3	3285	1603	1500	1365	135	430,410,370	272

It is evident from the titanium-chlorine stretching region for the compounds $[Ti_2Cl_7(O_2CR)(RCO_2H)]$ (R=Et, CMe_3) that both species contain two different types of

chlorine ligands, that is, terminal and bridging. Bands at 432, 415 and 369cm^{-1} (R=Et), and 430, 410 and 370cm^{-1} (R=CMe_3) are assigned to terminal chlorine-titanium stretching vibrations. As found previously with titanium tetrachloride adducts of the type [($TiCl_4$.L)$_2$] (L= monodentate ligand) the bridging chlorine ligands are identified by titanium-chlorine stretching vibrations at lower frequencies of 300-200cm^{-1}. For both of the compounds under discussion, [$Ti_2Cl_7(O_2CEt)(EtCO_2H)$] and [$Ti_2Cl_7(O_2CCMe_3)(Me_3CCO_2H)$], weak bands at 273 (R=Et) and 272cm^{-1} (R=CMe_3) may be attributed to υ(Ti-Cl) bridging vibrations.

^{1}H NMR Spectra for the species [$Ti_2Cl_7(O_2CR)(RCO_2H)$] (R=Et, CMe_3)

The ^{1}H NMR spectra for these compounds show broad multiplets in the region δ2.88-2.68 and 1.40-1.27 for [$Ti_2Cl_7(O_2CEt)(EtCO_2H)$], and a multiplet over the range δ1.49-1.13 in the spectrum of the trimethylacetate derivative, all corresponding to protons on the alkyl chain. As yet there is no convincing explanation for the complexity of the spectra in these regions but it may be possible that different conformers are present in solution. The ^{1}H NMR spectrum of [$Ti_2Cl_7(O_2CCMe_3)(Me_3CCO_2H)$] is shown in Figure 2.1.

The presence of a complexed acid molecule in these species is corroborated by the ^{1}H NMR spectra which show a broad resonance at δ9.81 (R=Et) and 10.30 (R=CMe_3), each due to the hydroxyl proton of the respective co-ordinated carboxylic acid.

2.4.2. Formation of the species [$Ti_2Cl_7(O_2CR)(RCO_2H)$] (R=Et, CMe_3)

It can be seen from the preceding discussion that the species [$Ti_2Cl_7(O_2CR)(RCO_2H)$] (R=Et, CMe_3) have been prepared and identified. Isolation of either product and subsequently heating in benzene for 2 hours at 60°C produced a very soluble compound which could not be isolated.

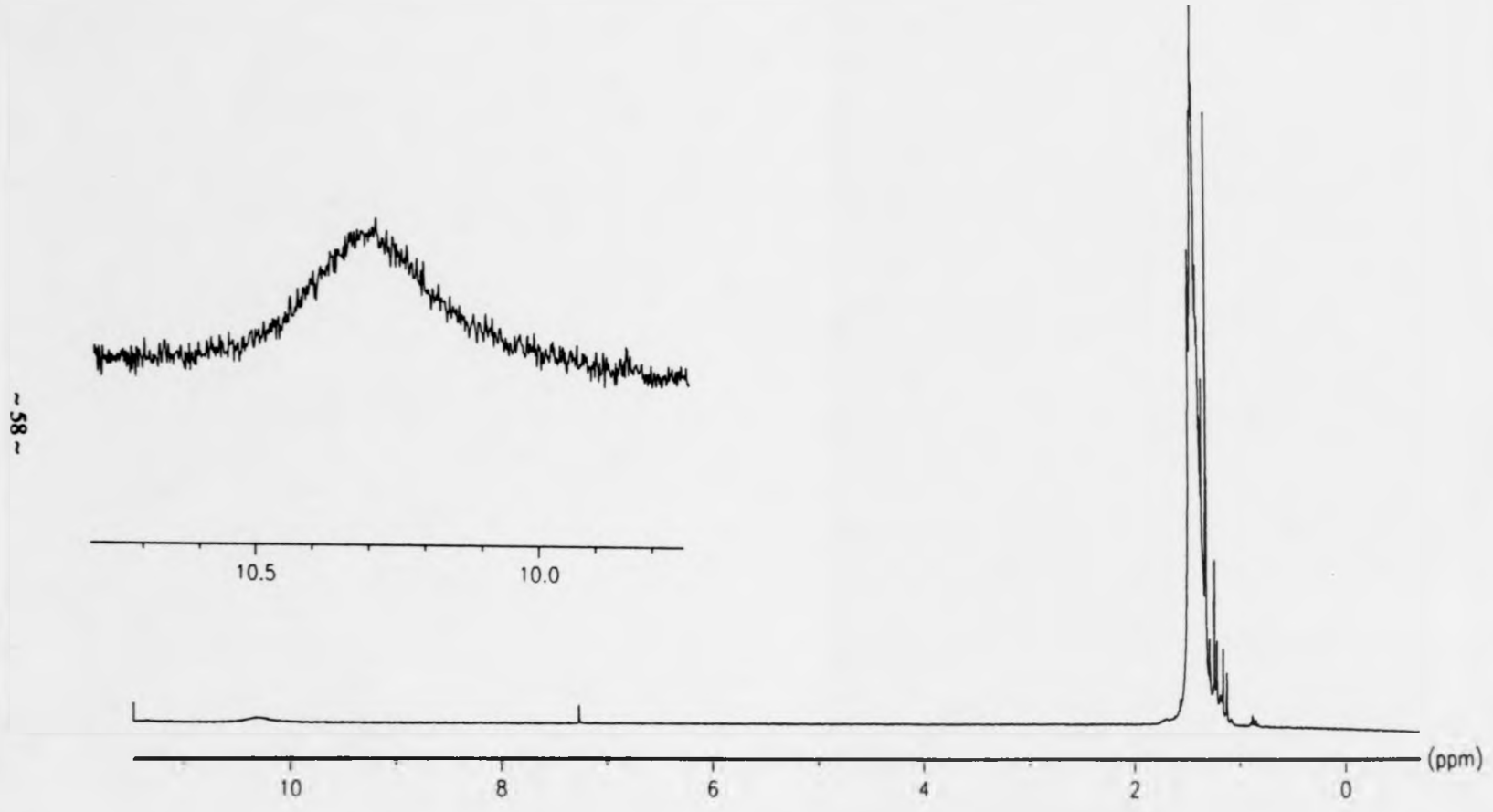


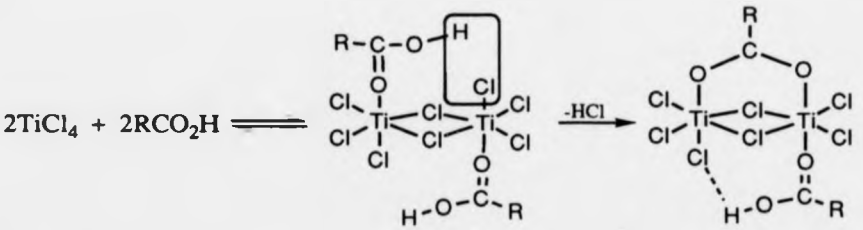
Figure 2.1 ^{1}H NMR spectrum of the compound $[Ti_2Cl_7(O_2CCMe_3)(Me_3CCO_2H)]$.

In previous experiments within these laboratories, heating the compound $[Ti_2Cl_7(O_2CC_6H_4Cl\text{-}p)(p\text{-}ClC_6H_4CO_2H)]$ in toluene to 55°C for 2 hours produced an orange solid which was identified by elemental analysis, ^1H NMR and IR spectra as $[TiCl_3(O_2CC_6H_4Cl\text{-}p)]$ thus giving support to the reaction scheme below.[188]

$$2TiCl_4 + 2p\text{-}ClC_6H_4CO_2H \longrightarrow [Ti_2Cl_7(O_2CC_6H_4Cl\text{-}p)(p\text{-}ClC_6H_4CO_2H)] + HCl$$

$$[Ti_2Cl_7(O_2CC_6H_4Cl\text{-}p)(p\text{-}ClC_6H_4CO_2H)] \xrightarrow{heat} 2[TiCl_3(O_2CC_6H_4Cl\text{-}p)] + HCl$$

The monocarboxylate species $[TiCl_3(O_2CR)]$ (R=Et, CMe_3) have been prepared previously by Amaudrut and co-workers and isolation of the compound has apparently not been met with difficulty.[174] It can only be concluded therefore, that on heating the species $[Ti_2Cl_7(O_2CR)(RCO_2H)]$ (R=Et, CMe_3), formation of the monocarboxylate did not occur on these occasions. Nevertheless, substantial evidence has already been presented in this thesis in favour of the compounds being the proposed co-ordinating acid species, and further work must be carried out to find out what the compound formed on heating is. These compounds may be envisaged as being prepared by the following route.



It is noteworthy that the second co-ordinating carboxylic acid chooses not to react with the nearest terminal chlorine on the adjacent titanium atom, to form a similar carboxylate bridge.[170] A possible reason for the stability of these derivatives may be deduced from the crystal structure analysis of the *para*-chlorobenzoic and crotonic acid derivatives which show that the configuration of a bridging carboxylate ligand across two titanium centres causes the Ti_2Cl_6 unit to bend in the centre therefore making it impossible for a second carboxylate to bridge the bent unit. The elimination of a second molecule of

HCl therefore only occurs at higher temperatures with the formation of the $[TiCl_3(O_2CR)]$ species. The fact that these compounds are trimeric rather than dimeric with two carboxylate groups bridging the two titanium atoms is consistent with the steric requirements of the bridging carboxylate group.

In comparison to the alkyl chain derivatives which have been prepared, i.e. propanoate and trimethylacetate, an analogous preparation was carried out using acetic acid. Initially, only oils were isolated which did not have the required elemental composition for the compound $[Ti_2Cl_7(O_2CMe)(MeCO_2H)]$. However, recent results from these laboratories tend to indicate that with careful choice of solvent, the species $[TiCl_3(O_2CR)]$ (R=Et, CMe_3) do form on heating $[Ti_2Cl_7(O_2CR)(RCO_2H)]$.

2.4.3. Preparation of Bis-Substituted Titanium Carboxylate species

We have so far seen that the reaction of $TiCl_4$ with carboxylic acids in a 1:1 mole ratio, may produce either the binuclear intermediate $[Ti_2Cl_7(O_2CR)(RCO_2H)]$ or the monocarboxylate $[TiCl_3(O_2CR)]$ depending upon the reaction conditions employed, as summarised below.

$$2TiCl_4 + 2RCO_2H \xrightarrow[\text{solvent}]{0\text{-}25^\circ C} [Ti_2Cl_7(O_2CR)(RCO_2H)] + HCl$$

$$TiCl_4 + RCO_2H \xrightarrow[\text{solvent}]{50\text{-}100^\circ C} [TiCl_3(O_2CR)] + HCl$$

(R=alkyl, aryl)

Further substitution of the chlorine ligands of the titanium monocarboxylate has been shown to occur at ambient temperature by increasing the molar concentration of the carboxylic acid as indicated by the equation below.[174,175,181]

$$TiCl_4 + 2RCO_2H \xrightarrow[\text{solvent}]{25^\circ C} [TiCl_2(O_2CR)_2] + 2HCl$$

(R=alkyl, aryl)

This is in sharp contrast to the formation of the monocarboxylate species which require temperatures in excess of 50°C for their preparation.[170] It was also suggested,

from molecular weight studies in benzene, that the bis-carboxylate species $[TiCl_2(O_2CR)_2]$ (R=Me, Et, CMe_3, CH_2Cl, $CHCl_2$), were dimeric in solution.[175] In addition to this information, the IR spectral data of the compounds indicated three carboxylate bands were present in the region 1300-1700cm^{-1}, and this was taken to imply the presence of two different types of bonding mode of the carboxylate groups. Based on these findings, a model **(2.7)** was proposed for species of the type $[TiCl_2(O_2CR)_2]$.

No structural characterisation of these compounds has so far been carried out, and therefore the actual arrangement of ligands around the titanium metal centre is unknown. Elemental analyses of the compounds in question has confirmed that the ratio of titanium to carboxylate ligand is 1:2. Due to the deficiency of structural data in this category of compounds, it was thought to be of interest to synthesise some of the bis-carboxylate species with the hope of obtaining a crystalline product suitable for X-ray diffraction studies. With this then established, a greater understanding of the $TiCl_4$-carboxylic acid system would be acquired. It must be added, that carboxylate species of the type $[TiCl_3(O_2CR)]$, and also those under discussion here of the proposed formulation $[TiCl_2(O_2CR)_2]$, have been found to be catalytically active in the polymerisation of alkenes when used in conjunction with a trialkylaluminium activator.[190] It would therefore be advantageous to be able to compare the effectiveness of polymerisation reactions by these systems with the changing structural features of the titanium carboxylate.

Propanoic and trimethylacetic acids have both been found to form species of the type $[Ti_2Cl_7(O_2CR)(RCO_2H)]$ and $[TiCl_3(O_2CR)]$ with $TiCl_4$ when a 1:1 molar ratio of reactants is used. Extending this work further, this thesis now reports the preparation and structural characterisation of species formed by the addition of a further mole of RCO_2H (R=Me, Et, CMe_3) to the reactant solution

Preparation of $[\{TiCl_2(O_2CR)(RCO_2H)\}_2O]$ (R=Me, Et, CMe_3)

Initial experiments were carried out using a reactant ratio of 1:2 (Ti:carboxylic acid) in the hope of obtaining the bis-carboxylate species $[TiCl_2(O_2CR)_2]$, although subsequently, the ratio was modified to 1:2.5 for reasons outlined in the following discussion.

Thus $TiCl_4$ (1 mol) was added to a solution of the appropriate carboxylic acid (2 mol) in a suitable solvent at room temperature (R=Me, toluene; R=Et, carbon tetrachloride: R=CMe_3, petroleum ether). The solution was then stirred for 4-5 hours within which time a precipitate was produced in high yields (70-90%).

Elemental analyses and IR spectra of the prepared compounds tended initially to confirm the reported identification of the $[TiCl_2(O_2CR)_2]$ (R=Me, Et, CMe_3) species. However, the ^1H NMR spectrum for each of these compounds showed a broad singlet varying between δ9-11. Initially, it was presumed that a little hydrolysis was occurring in the sample solution while the NMR measurements were being taken, thus causing the production of the respective carboxylic acid. However, closer inspection of each of the IR spectra eliminated this possibility.

The presence of a weak, broad hydroxyl stretching band at *ca.* 3200cm^{-1} in the products again indicated the possibility of slight hydrolysis during the running of the spectrum, but since the respective free-acid carbonyl band at about 1710cm^{-1} was absent it appeared more likely that carboxylic acid ligands were co-ordinating to the titanium metal centres.

X-ray crystal structure analysis for R=Et and R=CMe_3 did not confirm the dimeric structure of $[TiCl_2(O_2CR)_2]$ which was previously proposed, but instead revealed the binuclear oxo bridged species $[\{TiCl_2(O_2CEt)(EtCO_2H)\}_2O]$ and $[\{TiCl_2(O_2CCMe_3)(Me_3CCO_2H)\}_2O]$ as discussed below. Spectral and analytical information also indicates the formation of $[\{TiCl_2(O_2CMe)(MeCO_2H)\}_2O]$ from the

reaction of acetic acid with $TiCl_4$, by comparison with the data of the other two compounds (R=Et, CMe_3).

Possible Routes to the Formation of $[\{TiCl_2(O_2CR)(RCO_2H)\}_2O]$ (R=Me, Et, CMe_3)

Repeated efforts to prepare the compounds $[TiCl_2(O_2CR)_2]$ (R=Me, Et, CMe_3) produced only species of the type $[\{TiCl_2(O_2CR)(RCO_2H)\}_2O]$ in high yield (70-90%). Initially, it was thought that during the course of the reaction, hydrolysis was occurring. Rigorous endeavours were therefore made to eliminate any water which may have been present in the carboxylic acid, solvent, or the nitrogen atmosphere, and it was confirmed that the reactions proceeded in the same way.

The reaction liquors which were isolated from the oxo bridged products were also investigated. IR spectral measurements showed the presence of the respective acid chlorides, RCOCl, (R=Me, Et, CMe_3) in each of the liquors. The acid chloride carbonyl stretching band was observed in the region of $1800cm^{-1}$.

From this information, it may be suggested that the species $[\{TiCl_2(O_2CR)(RCO_2H)\}_2O]$ appear to be formed by a reaction involving oxygen abstraction from a carboxylic acid molecule rather than a hydrolysis reaction. Similar reactions have been postulated previously for the titanium oxo clusters $[Ti_4O_2Cl_6(O_2CPh)_6]$[191] and $[Ti_3O_2Cl_3(O_2CC_6H_4Me\text{-}p)_5]$[192], even though the present compounds are obtained at room temperature while the oxo clusters require 100°C. These two possible reaction routes are summarised in the equations below.

Oxygen abstraction route

$$2TiCl_4 + 5RCO_2H \xrightarrow[\text{solvent}]{25^\circ C} [\{TiCl_2(O_2CR)(RCO_2H)\}_2O] + RCOCl + 3HCl$$

(R=Me, Et, CMe_3)

Hydrolytic route

$$2TiCl_4 + 4RCO_2H + H_2O \xrightarrow[\text{solvent}]{25^{\circ}C} [\{TiCl_2(O_2CR)(RCO_2H)\}_2O] + 4HCl$$

(R=Me, Et, CMe_3)

Further support for the oxygen abstraction route comes from the fact that optimum yields of the species $[\{TiCl_2(O_2CR)(RCO_2H)\}_2O]$ (80-90% prior to recrystallisation) are obtained using a 1:2.5 (Ti: acid) ratio rather than a 1:2 mole ratio of reactants.

It should be noted that analogous oxo bridged titanium(IV) compounds have been previously isolated in this laboratory using controlled hydrolysis reactions. Thus the hydrolysis of $[TiCl_3(O_2CPh)]$ in ethyl acetate or tetrahydrofuran yields the oxo derivatives $[\{TiCl_2(O_2CPh)L\}_2O]$ (L=$MeCO_2Et$ or THF) in good yield, with the evolution of HCl.[193] This stoichiometry is comparable with the compounds isolated in this thesis, where for the latter formulation R=Me, Et, CMe_3 and L=$MeCO_2H$, $EtCO_2H$, Me_3CCO_2H. While this hydrolytic reaction appeared to occur with most species of the type $[TiCl_3(O_2CR)]$, the yield of isolable oxo compound varied. Indeed, with R=CMe_3, only low yields were obtained, but R=Me produced moderate yields of 40-50%.

In summary, the reaction of $TiCl_4$ with acetic, propanoic or trimethylacetic acid has now produced new species of the formulation $[\{TiCl_2(O_2CR)(RCO_2H)\}_2O]$ in high yield (~ 70% after recrystallisation) by a clean, direct, and non-hydrolytic route.

IR Spectra of the species $[\{TiCl_2(O_2CR)(RCO_2H)\}_2O]$ (R=Me, Et, CMe_3)

The IR spectra of the species $[\{TiCl_2(O_2CR)(RCO_2H)\}_2O]$ (R=Me *1*, Et *2*, CMe_3 *3*) show similar major absorption bands in the region 4000-200cm^{-1}. The IR spectra of these compounds within the range of 2000-300cm^{-1} have been previously published by Amaudrut and co-workers, although, as discussed previously, the products were wrongly formulated as $[TiCl_2(O_2CR)_2]$.[175]

A strong feature in all three spectra is the broad band centred around 3200cm^{-1} which can be assigned to a hydrogen-bonded hydroxyl group, rather like that found in the

spectrum of the corresponding carboxylic acid. This is the first indication of the presence of acid molecules co-ordinated to the titanium metal centre. It should be noted, that this broadness is in contrast to the hydroxyl stretching band of the $[Ti_2Cl_7(O_2CR)(RCO_2H)]$ (R=Et, CMe_3) species which appears sharper and at higher wavenumbers. This would tend to indicate that hydrogen bonding in the latter compounds is weaker than that present in the oxo bridged species *1*, *2* and *3*.

The free acid carbonyl absorption band at 1714 *1*, 1718 *2* and 1704cm^{-1} *3* is absent in each of the spectra of the oxo compounds, and is replaced by a strong absorption band at 1655 *1* and 1650cm^{-1} *2* and *3*, indicating a decrease in wavenumber of 59 *1*, 68 *2* and 54cm^{-1} *3*. This shift to lower wavenumber of the carboxylic acid carbonyl group is indicative of co-ordination of the acid to the titanium centre through the carbonyl oxygen rather than the C-OH group.

A similar decrease in wavenumber of the carbonyl absorption band was reported by Mach and Drahorádová in the investigation of $TiCl_4$-carboxylic acid adducts.[169] The carbonyl stretching band of the free acid (*ca.* 1700cm^{-1}) decreased in wavenumber by approximately 50cm^{-1} on co-ordination to the metal centre whilst in solution.

The hydroxyl and carbonyl stretching bands for acid co-ordination to the titanium metal centre are also in line with those found in the IR spectra of the vanadium(II) complexes $[VCl_2(MeCO_2H)_4]$ (i) and $[V(MeCO_2H)_6]Br_2$ (ii).[194] The hydroxyl absorption bands were found to be broad, of medium intensity, and situated at 3340cm^{-1} (i) and 3170cm^{-1} (ii) whilst the carbonyl bands were strong and sharp, and positioned at 1675 (i) and 1655cm^{-1} (ii), indicating a shift from the free acid carbonyl stretching band of 39cm^{-1} for (i) and 59cm^{-1} for (ii).

The carbonyl absorption bands of the co-ordinating acid in *1*, *2* and *3* occur at higher wavenumbers than the compounds $[Ti_2Cl_7(O_2CR)(RCO_2H)]$ (R=Et, CMe_3, Table 2.5; R=*p*-haloC_6H_4, Table 2.1) possibly signifying that the Ti-carbonyl bond is stronger in the latter compounds than the oxo bridged species. Therefore the titanium atom in the $[Ti_2Cl_7(O_2CR)(RCO_2H)]$ compounds is a better acceptor of the carbonyl group, and

possibly the acid is co-ordinated more strongly and less susceptible to replacement with another donor molecule such as THF or ethyl acetate. It will be seen in the following chapter that the co-ordinated acid in the compounds *1*, *2*, and *3* has the ability to be replaced by THF donor ligands to give the compounds $[\{TiCl_2(O_2CR)THF\}_2O]$ in virtually quantitative yield. Preliminary experiments carried out using $[Ti_2Cl_7(O_2CR)(RCO_2H)]$ (R=Et, CMe_3) did not produce the analogous THF adduct $[Ti_2Cl_7(O_2CR)THF]$. Only oils which could not be identified from elemental analyses and IR data were isolated.

The carboxylate stretching bands of the compounds *1*, *2* and *3* are shown in Table 2.6, along with other pertinent IR data.

Table 2.6 Major IR bands (cm^{-1}) of the titanium(IV) species $[\{TiCl_2(O_2CR)(RCO_2H)\}_2O]$ (R=Me, Et, CMe_3).

R	υ(C=O) free acid	υ(C=O) co-ord.acid	$\upsilon(COO)_{asym}$	$\upsilon(COO)_{sym}$	Δ	υ(Ti-O-Ti)	υ(Ti-Cl) terminal
Me	1714	1655	1540	1430	110	733	430, 410 380, 350
Et	1718	1650	1520	1405	115	736	430, 415 370
CMe_3	1704	1650	1525	1418	107	733	451,405 390,375

The carboxylate absorption band positions in the IR spectra are in accord with those found in titanium carboxylate species containing bridging systems such as $[Ti_2Cl_7(O_2CR)(RCO_2H)]$ (R=Et, CMe_3, CH=CHMe, *p*-haloC_6H_4) and $[TiCl_3(O_2CR)]$ (R=Me, Et, CMe_3, Ph, *p*-MeC_6H_4).[170]

The Δ value has been discussed in the previous chapter and although it must be viewed tentatively, it may be used as an assignment for the bonding mode of the carboxylate ligand. Values of around $110cm^{-1}$ as observed for the (μ_2-O) species reported here, would be indicative of a bidentate chelating or a bridging mode of co-

ordination.[117] From crystal structure determination of the species $[\{TiCl_2(O_2CEt)(EtCO_2H)\}_2O]$ and $[\{TiCl_2(O_2CCMe_3)(Me_3CCO_2H)\}_2O]$ it has been confirmed that the carboxylate ligands are indeed bridging, thus giving evidence to the viability of this technique in the identification of carboxylate bonding modes.

Table 2.7 notes the carboxylate stretching frequencies of the structurally analogous compounds $[\{TiCl_2(O_2CR)L\}_2O]$ (R=Me, CMe_3, Ph; L=$MeCO_2Et$ and THF) which have been prepared previously from this laboratory, by the hydrolysis of the $[TiCl_3(O_2CR)]$ derivatives, and identified by X-ray diffraction study of $[\{TiCl_2(O_2CPh)(MeCO_2Et\}_2O]$.[193,195]

Table 2.7 IR spectral information (cm^{-1}) concerning the species $[\{TiCl_2(O_2CR)L\}_2O]$.[195]

Compound		υ(C=O) free ester	υ(C=O) co-ord.ester	$\upsilon(COO)_{asym}$	$\upsilon(COO)_{sym}$	Δ	υ(Ti-O-Ti)
R=Me	L=$MeCO_2Et$	1741	1655	1540	1410	130	720
	L=THF	-	-	1550	1410	140	750
R=CMe_3	L=$MeCO_2Et$	1741	1665	1520	1420	100	720
	L=THF	-	-	1525	1420	105	720
R=Ph	L=$MeCO_2Et$	1741	1650	1520	1410	110	720
	L=THF	-	-	1520	1410	110	720

It can be seen that the strong, sharp, asymmetric and symmetric carboxylate stretching frequencies are comparable to those of the related co-ordinated acid species (Table 2.6). Further to this, the Δ values (*ca.* 115 cm^{-1}) confirm the presence of bridging carboxylate groups.

One further similarity in the IR spectra of these compounds occurs in the region 750-700cm^{-1}. Here the Ti-O-Ti absorption band may be observed as a strong, broad, signal and appears at 733 *1*, 736 *2* and 733cm^{-1} *3*. The region 900-600cm^{-1} in the IR spectra of *1*, *2*, and *3* is shown in Figure 2.2, overleaf.

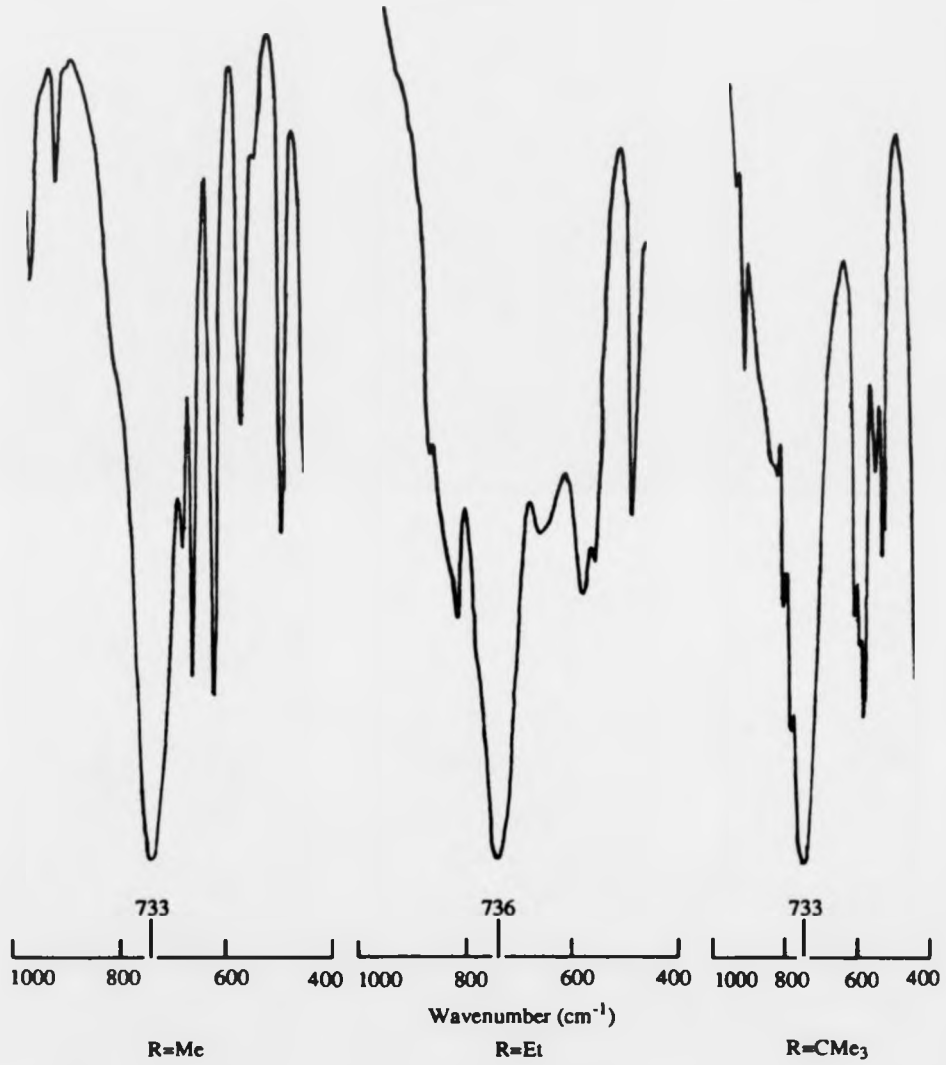


Figure 2.2 The broad, strong Ti-O-Ti stretching bands in the IR spectra of the species $[\{TiCl_2(O_2CR)(RCO_2H)\}_2O]$ (R=Me, Et, CMe_3).

An identical strong band has been reported for the ethyl acetate and THF analogues (Table 2.7) which is situated *ca.* 720cm^{-1}.

All the Ti-Cl bonds in *1*, *2*, and *3* are terminal and strong bands appearing in the region 450-350cm^{-1} are assigned to Ti-Cl stretching vibrations, *viz.* 430, 410, 380, 350 *1*, 430, 415, 370, *2* and 451, 405, 390, 375cm^{-1} *3*.

IR Studies of Metal Carboxylates which contain the $[M_2(\mu_2\text{-}O)(\mu_2\text{-}O_2CR)_2]^{n+}$ core.

A variety of titanium oxo species have been prepared by the reaction of a non oxo bridged compound with water and the hydrolysis of a titanium halide bond is often involved.[196] These compounds will be discussed in more detail in subsequent chapters. The oxygen atom may be terminal (e.g. Ti=O) or bridging (e.g. Ti-O-Ti). However relatively few compounds are known with terminal Ti=O bonds, and the majority of titanium oxo compounds contain a (μ_2-O) moiety as is demonstrated by the compounds $[\{TiCl_2(O_2CR)(RCO_2H)\}_2O]$ (R=Me, Et, CMe_3) which have been prepared as reported in this chapter, through a non-hydrolytic route.

For the oxo bridging compounds, where fully characterised by X-ray diffraction, bridging distances vary between the values for M=O linkages and 'pure' single M-O bonds. This is indicative of some degree of double bond character in the bridging bonds due to M(dπ)-O(pπ)-M(dπ) overlap. This overlap is maximised in a linear arrangement where the M-O bonds are seen to be shorter than in the systems containing bent M-O-M bridges.[196]

Oxo bridged complexes are formed for a variety of metal atoms with great facility and with a wide variety of ligands. Carboxylate supported binuclear metal species having a core of $[M_2(\mu_2\text{-}O)(\mu_2\text{-}O_2CR)_2]^{n+}$ have been widely found for metals such as Fe^{III}, Ru^{III}, V^{III}, Mn^{III}. Lippard *et al*[197] and Wieghardt and co-workers[198] have separately developed model compounds for species involved in a variety of processes, especially redox, in biological systems. In particular, model compounds for the haemerythin core have been developed which contain Fe-O-Fe units supported by carboxylate bridges and

contain tridentate ligands capable of co-ordinating in the *fac* mode to each metal ion. These compounds have generally been prepared by hydrolytic reactions.

Related compounds which contain monodentate terminal ligands are few, but have been found for $[\{Os(O_2CMe)Cl_2(PPh_3)\}_2O]$,[199] $[\{Nb(O_2CPh)Cl_3\}_2O]$,[200] $[\{Ru(O_2CMe)Py_3\}_2O](PF_6)_2$[201] and $[\{Ru(MeCN)_2(O_2CMe)(PPh_3)\}_2O](ClO_4)_2$.[202] Structural information concerning (μ_2-O) systems with bidentate and tridentate ligands is far more abundant. In addition to the homonuclear metal systems described briefly, mixed metal dinuclear complexes such as $[FeOMn(O_2CMe)_2(Me_3TACN)(TACN)](ClO_4)_3$ and $[CrOFe(O_2CMe)_2(Me_3TACN)(TACN)](PF_6)_2$ have been isolated.[203]

In order to obtain information about the Fe-O-Fe stretching vibrations in the IR of (μ-oxo)di-iron(III) complexes the spectra of $[\{Fe(O_2CMe)(HBpz_3)\}_2{}^{16}O]$ and $[\{Fe(O_2CMe)(HBpz_3)\}_2{}^{18}O]$ samples were investigated and it is worth noting the conclusions here as a comparison with the Ti(IV) compounds.[197] From the results it is evident that the $\upsilon(Fe\text{-}O\text{-}Fe)_{asym}$ mode shifts from 751 (^{16}O) to 721cm^{-1} (^{18}O) upon isotopic substitution. The low intensity and energy of the bands was proposed to be a result of the small Fe-O-Fe angle of 123.6°, since the change in the dipole moment diminishes for this vibrational mode when the M-O-M angle decreases, thus reducing the intensity of the asymmetric stretching band. The authors also suggest that this was a factor in the lack of assignment of the asymmetric μ-oxo stretching mode by Walton *et al* of the osmium complex $[\{Os(O_2CMe)Cl_2(PPh_3)\}_2O]$.[204]

Some spectral information for compounds having the $[M_2(\mu_2\text{-}O)(\mu_2\text{-}O_2CR)_2]^{n+}$ core is given in Table 2.8. Although the data is drawn from a variety of metal centres, the information serves to illustrate the Δ values $[\upsilon(COO)_{asym}\text{-}\upsilon(COO)_{sym}]$ which lie in the range 100-150cm^{-1}, indicating a symmetrical bridging carboxylate co-ordination, as discussed in Chapter 1.

Table 2.8 IR data (cm^{-1}) for some compounds containing the $[M_2(\mu_2\text{-}O)(\mu_2\text{-}O_2CR)_2]^{n+}$ core.

Compound	$\upsilon(COO)_{asym}$	$\upsilon(COO)sym$	Δ	$\upsilon(M\text{-}O\text{-}M)$	Ref.
$[\{NbCl_3(O_2CPh)\}_2O]$	1494	1407	87	a	200
$[\{NbCl_3(O_2CC_6H_4o\text{-}F)\}_2O]$	1494	1403	91	a	200
$[\{Fe(O_2CMe)(HBpz_3)\}_2O]$	1560	1427	133	751	197
$[\{Fe(O_2CMe)(TACN)\}_2O]I_2$ 0.5MeCN	a	a	-	749	205
$[\{V(O_2CMe)(Me_3TACN)\}_2O]I_2.\ H_2O$	1560	1468	92	670	206
		1430	130		
$[\{Ti(O_2CPh)(Me_3TACN)\}_2O](PF_6)_2$	1541	1397	144	685	207

[a] unreported

TACN 1,4,7-triazacyclononane
Me_3TACN 1,4,7-trimethyl-1,4,7-triazacyclonanane
$HBpz_3$ Tri-1-pyrazolylborate ion

^1H NMR Spectra of $[\{TiCl_2(O_2CR)(RCO_2H)\}_2O]$ (R=Me, Et, CMe_3)

The ^1H NMR data of the title compounds show multiplets in the region associated with the alkyl protons of both the carboxylate ligand and the co-ordinated carboxylic acid.

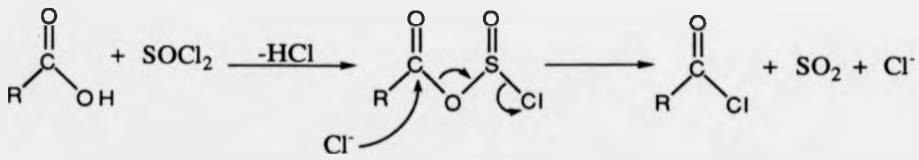
For the acetate derivative $[\{TiCl_2(O_2CMe)(MeCO_2H)\}_2O]$, the multiplet spans the range δ2.20-1.93. Due to its low solubility in chlorinated or aromatic solvents, deuterated acetonitrile was used for the NMR measurements. The solvent molecules most probably exchange with the co-ordinated acid ligands to produce the compound $[\{TiCl_2(O_2CMe)(CD_3CN)\}_2O]$ and free acetic acid, and therefore the multiplet centred at δ2.07 consists of both acetate ligand and acetic acid protons which overlap with the residual protons of the deuterated acetonitrile solvent. The hydroxyl proton of the free acetic acid is observed at δ8.8 and is less broad than the corresponding signals in the spectra of the propanoate and trimethylacetate derivatives.

The spectrum of the propanoate derivative (in $CDCl_3$) gives two multiplets at δ2.65-2.47 and 1.36-1.20 which are attributable to the methylene and methyl protons respectively of both the propanoate ligand and the co-ordinated propanoic acid. The hydroxyl proton signal is broad but is observed at δ11.3.

With the trimethylacetate derivative $[\{TiCl_2(O_2CCMe_3)(Me_3CCO_2H)\}_2O]$ similarly the spectrum (in $CDCl_3$) shows the presence of a multiplet at δ1.37-1.20 and the hydroxyl proton is observed as a broad signal at δ11.3. The ^{13}C NMR spectrum of $[\{TiCl_2(O_2CCMe_3)(Me_3CCO_2H)\}_2O]$ is straightforward, showing two sets of resonances from the co-ordinated carboxylate and acid moieties at δ26 and 27, and δ39 and 40 from the methyl groups and the single carbon atom of the CMe_3 groups respectively. The resonance from both the carboxylate carbons occurs at δ189.5.

2.4.4. A Possible Mechanism for the Formation of the Binuclear Oxo Species of the formulation $[\{TiCl_2(O_2CR)(RCO_2H)\}_2O]$ (R=Me, Et, CMe_3)

It is interesting to note at this point the general preparation of acid chlorides from the respective carboxylic acids which have been carried out in industry, and in the laboratory.[208] The most widely used synthesis of acid chlorides is based on the reaction of a free carboxylic acid with thionyl chloride as shown by the following reaction scheme.

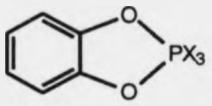


The reactivity towards thionyl chloride is such that there is a correlation with the acidity of the acids; the stronger the acid, the less reactive it becomes.

The phosphorus chlorides PCl_3, PCl_5 and $POCl_3$ are common reagents for preparing acid chlorides of a variety of carboxylic acids but often the reactions are

sluggish. Modifications of these phosphorus halides have allowed better yields to be obtained.

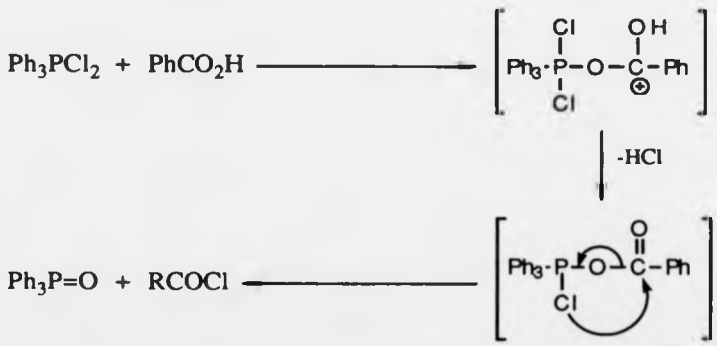
$[PX_3(O_2C_6H_4)]$ (X=Cl, Br) **(2.11)** and $[Ph_3PX_2]$ (X=Cl, Br) have been used successfully in the preparation of a number of aromatic and aliphatic acid halides. These reactions can be carried out at room temperature or slightly above, and convert carboxylic acids or anhydrides in good yields to the acid halides.



X=Cl, Br

(2.11)

The proposed reaction between Ph_3PCl_2 and benzoic acid to produce benzoyl chloride is shown below.[209]



These findings may be applied to the preparation of the titanium(IV) oxo carboxylate species. A possible reaction mechanism is shown in Figure 2.3 overleaf.

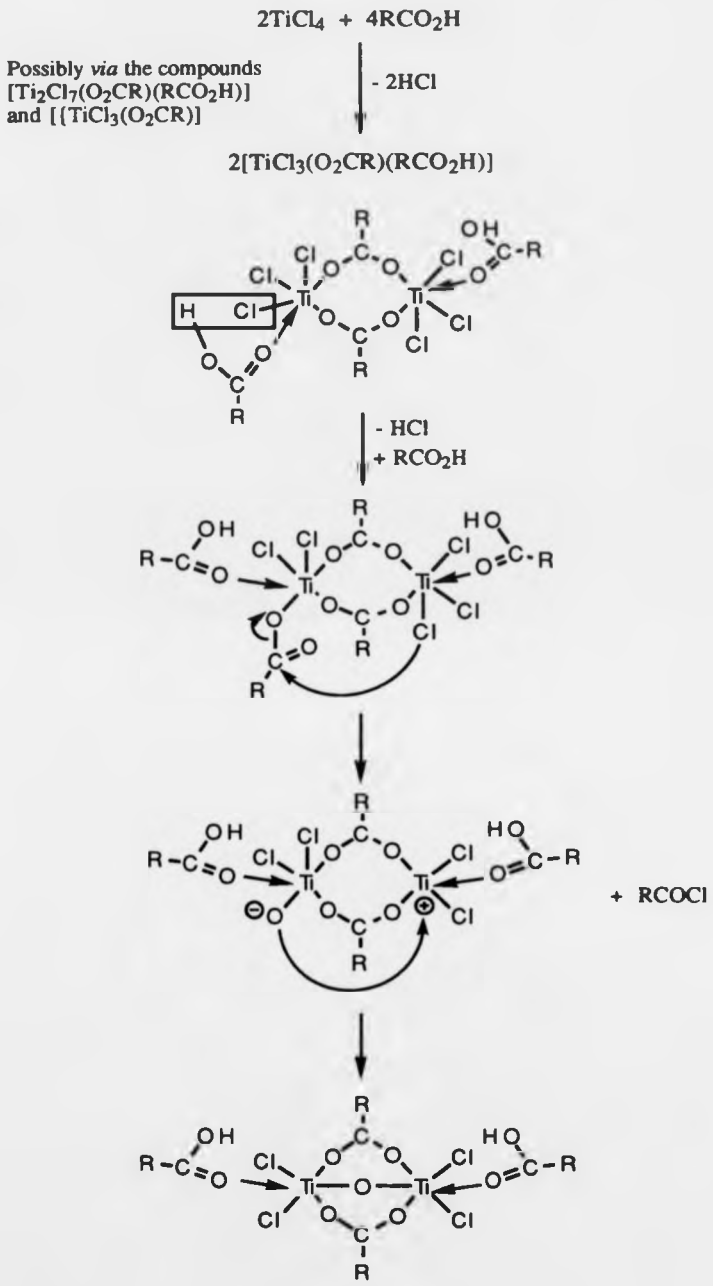


Figure 2.3 A possible reaction mechanism for the formation of species of the type $[\{TiCl_2(O_2CR)(RCO_2H)\}_2O]$ (R=Me, Et, CMe_3)

2.4.5. The X-Ray Crystal Structures of the Binuclear Titanium Carboxylate species $[\{TiCl_2(O_2CEt)(EtCO_2H)\}_2O]$ and $[\{TiCl_2(O_2CCMe_3)(Me_3CCO_2H)\}_2O]$

Single crystals of both of the title compounds were obtained as colourless shards from solutions of the respective dinuclear species in dichloromethane layered with light petroleum. The crystals were obtained after approximately one week as the slow diffusion occurred. Suitable crystals were sealed under argon in 0.5mm diameter glass capillary tubes, and X-ray crystallographic studies were then carried out.

The structure of $[\{TiCl_2(O_2CEt)(EtCO_2H)\}_2O]$ is shown in Figure 2.4, and selected bond lengths and angles are displayed in Tables 2.9 and 2.10 respectively. The structure of the trimethylacetate derivative $[\{TiCl_2(O_2CCMe_3)(Me_3CCO_2H)\}_2O]$ is analogous to that of the propanoate and is displayed in Figure 2.5. Selected bond lengths and angles for this structure are presented in Tables 2.11 and 2.12 respectively. Because of the disorder, the dimensions are of comparatively low accuracy for this latter structure, but are typical for these dinuclear species.

As can be seen by reference to Figure 2.4 and 2.5, the compounds are isostructural, both containing the characteristic μ_2-oxo-bis-μ_2-carboxylate dinuclear fragment which has already been found for a number of other metals.

For both compounds $[\{TiCl_2(O_2CR)(RCO_2H)\}_2O]$ (R=Et, CMe_3) the two titanium atoms show a near octahedral co-ordination. The metal atoms are linked by two symmetrically bridging carboxylate ligands and a μ_2-O unit, with the remaining three non-bridging positions on each metal being occupied by the two chlorine atoms and an acid molecule which is *trans* to the μ_2-O group, and co-ordinated through the carbonyl moiety.

Previously, this laboratory has reported the related compounds $[Ti_2(\mu_2\text{-}O)(\mu_2\text{-}O_2CPh)_2Cl_4.2L]$ (L=$MeCO_2Et$ or THF) which were obtained by hydrolysis reactions, and these also have the ligand *trans* to the bridging oxygen atom.[193]

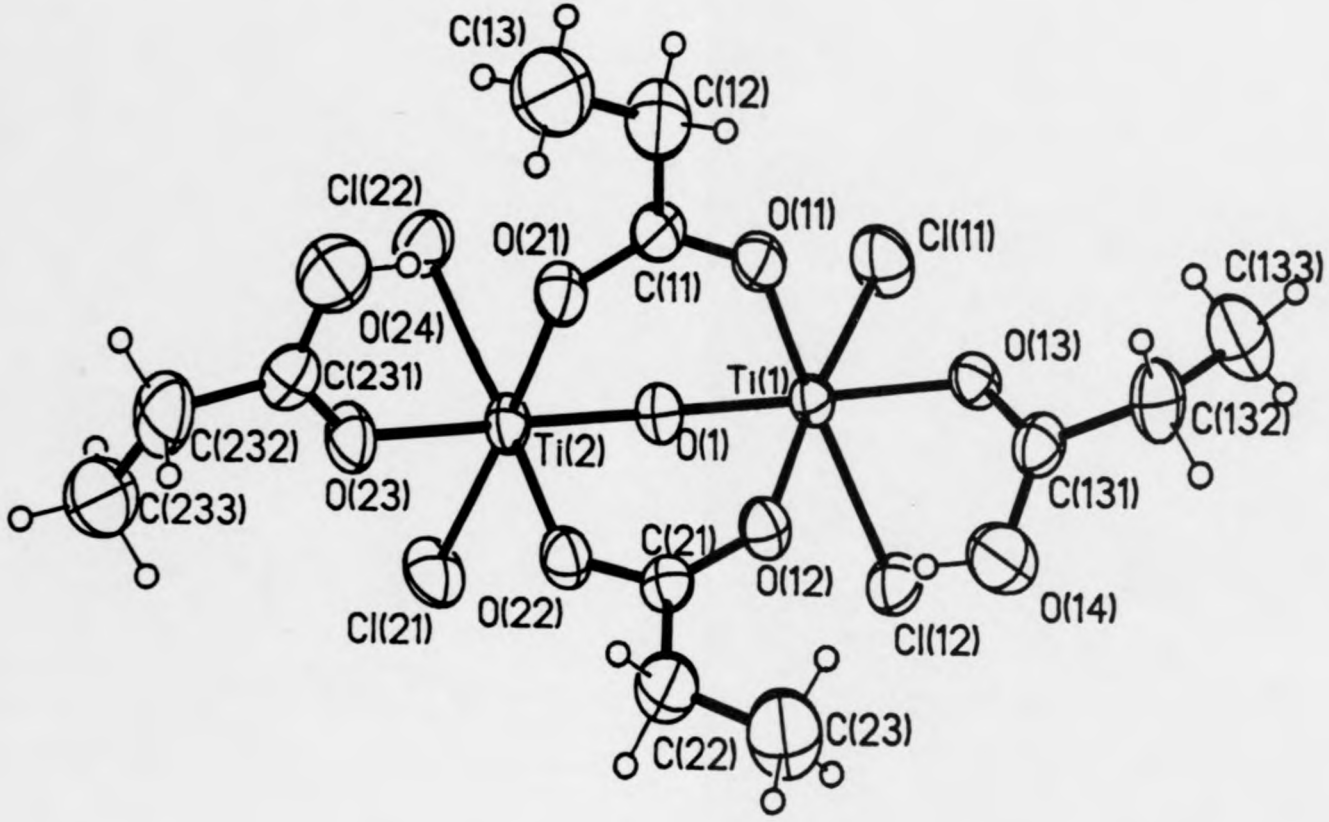


Figure 2.4 The X-ray crystal structure of the compound $[\{TiCl_2(O_2CEt)(EtCO_2H)\}_2O]$

Table 2.9 Selected bond lengths for [{$TiCl_2(O_2CEt)(EtCO_2H)\}_2O$)] (Å)

Ti(1)-Ti(2)	3.340(2)	Ti(1)-Cl(11)	2.237(1)
Ti(1)-Cl(12)	2.276(1)	Ti(1)-O(1)	1.795(3)
Ti(1)-O(11)	1.995(3)	Ti(1)-O(12)	2.128(2)
Ti(1)-O(13)	2.112(3)	Ti(2)-Cl(21)	2.236(1)
Ti(2)-Cl(22)	2.280(1)	Ti(2)-O(1)	1.792(3)
Ti(2)-O(21)	2.128(3)	Ti(2)-O(22)	1.992(3)
Ti(2)-O(23)	2.077(3)	O(11)-C(11)	1.264(5)
O(12)-C(21)	1.269(4)	O(13)-C(131)	1.221(4)
O(14)-C(131)	1.317(5)	O(21)-C(11)	1.256(5)
O(22)-C(21)	1.253(5)	O(23)-C(231)	1.209(6)
O(24)-C(231)	1.317(6)		

Table 2.10 Selected bond angles for [{$TiCl_2(O_2CEt)(EtCO_2H)$}$_2$O] (°)

Cl(11)-Ti(1)-Cl(12)	96.5(1)	Cl(11)-Ti(1)-O(1)	98.0(1)
Cl(12)-Ti(1)-O(1)	99.1(1)	Cl(11)-Ti(1)-O(11)	94.0(1)
Cl(12)-Ti(1)-O(11)	164.6(1)	O(1)-Ti(1)-O(11)	90.6(1)
Cl(11)-Ti(1)-O(12)	172.6(1)	Cl(12)-Ti(1)-O(12)	84.4(1)
O(1)-Ti(1)-O(12)	89.1(1)	O(11)-Ti(1)-O(12)	83.7(1)
Cl(11)-Ti(1)-O(13)	90.5(1)	Cl(12)-Ti(1)-O(13)	88.6(1)
O(1)-Ti(1)-O(13)	167.8(1)	O(11)-Ti(1)-O(13)	80.0(1)
O(12)-Ti(1)-O(13)	82.2(1)	Cl(21)-Ti(2)-Cl(22)	97.7(1)
Cl(21)-Ti(2)-O(1)	97.8(1)	Cl(22)-Ti(2)-O(1)	98.7(1)
Cl(21)-Ti(2)-O(21)	172.9(1)	Cl(22)-Ti(2)-O(21)	84.1(1)
O(1)-Ti(2)-O(21)	88.7(1)	Cl(21)-Ti(2)-O(22)	94.3(1)
Cl(22)-Ti(2)-O(22)	163.7(1)	O(1)-Ti(2)-O(22)	90.5(1)
O(21)-Ti(2)-O(22)	82.7(1)	Cl(21)-Ti(2)-O(23)	90.5(1)
Cl(22)-Ti(2)-O(23)	88.0(1)	O(1)-Ti(2)-O(23)	168.6(1)
O(21)-Ti(2)-O(23)	82.7(1)	O(22)-Ti(2)-O(23)	80.9(1)
Ti(1)-O(1)-Ti(2)	137.3(1)	Ti(1)-O(11)-C(11)	133.3(2)
Ti(1)-O(12)-C(21)	132.4(2)	Ti(1)-O(13)-C(131)	139.0(2)
Ti(2)-O(21)-C(11)	132.3(3)	Ti(2)-O(22)-C(21)	134.5(2)
Ti(2)-O(23)-C(231)	141.4(3)	O(11)-C(11)-O(21)	123.7(3)
O(12)-C(21)-O(22)	123.4(3)	O(13)-C(131)-O(14)	121.5(4)
O(23)-C(231)-O(24)	121.3(4)		

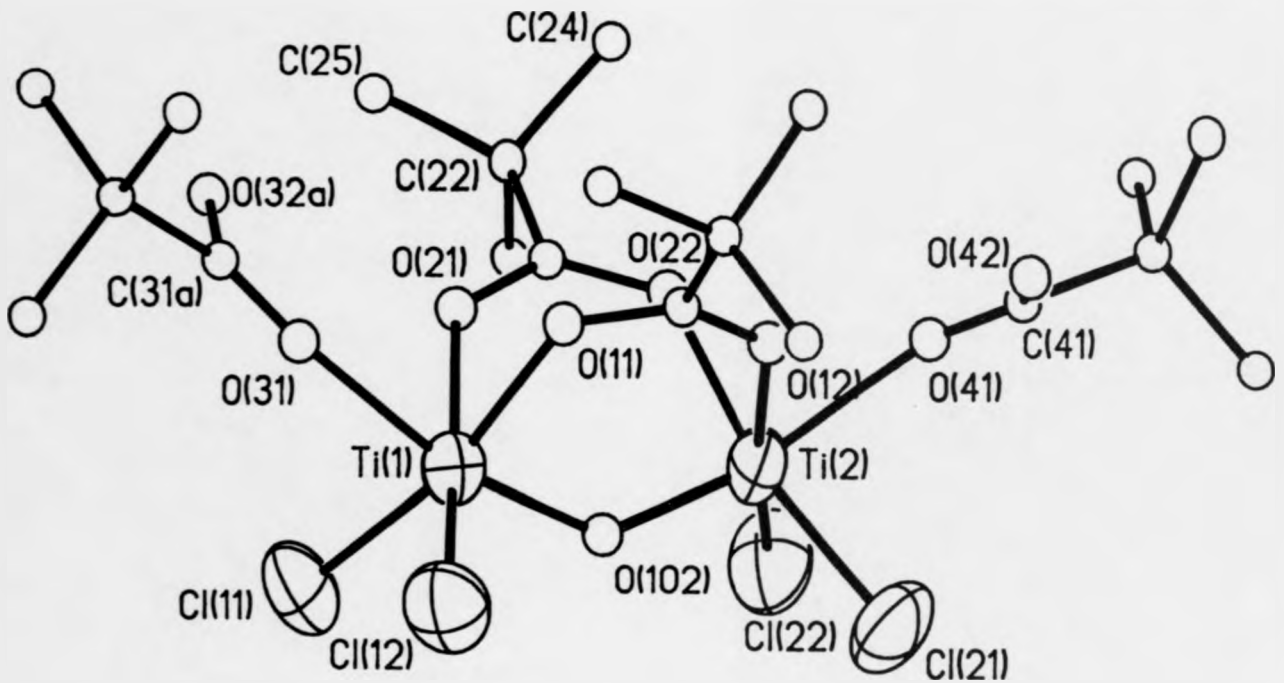


Figure 2.5 The X-ray crystal structure of the compound $[\{TiCl_2(O_2CCMe_3)(Me_3CCO_2H)\}_2O]$

Table 2.11 Selected bond lengths for $[\{TiCl_2(O_2CCMe_3)(Me_3CCO_2H)\}_2O]$ (Å)

Ti(1)-Ti(2)	3.307(7)	Ti(1)-Cl(11)	2.260(8)
Ti(1)-Cl(12)	2.259(8)	Ti(1)-O(102)	1.772(15)
Ti(1)-O(11)	2.055(14)	Ti(1)-O(21)	2.060(15)
Ti(1)-O(31)	2.085(17)	Ti(2)-Cl(21)	2.275(8)
Ti(2)-Cl(22)	2.255(9)	Ti(2)-O(102)	1.766(15)
Ti(2)-O(12)	2.090(16)	Ti(2)-O(22)	1.991(15)
Ti(2)-O(41)	2.138(18)	O(11)-C(11)	1.224(27)
O(12)-C(11)	1.251(27)	O(21)-C(21)	1.265(35)
O(22)-C(21)	1.263(31)	O(31)-C(31a)	1.108(38)
O(31)-C(31b)	1.146(50)	O(32a)-C(31a)	1.419(43)
O(32b)-C(31b)	1.432(90)	O(41)-C(41)	1.113(39)
O(42)-C(41)	1.438(50)		

Table 2.12 Selected bond angles for $[\{TiCl_2(O_2CCMe_3)(Me_3CCO_2H)\}_2O]$ (°)

Cl(11)-Ti(1)-Cl(12)	97.8(3)	Cl(11)-Ti(1)-O(102)	100.1(5)
Cl(12)-Ti(1)-O(102)	99.3(5)	Cl(11)-Ti(1)-O(11)	168.0(5)
Cl(12)-Ti(1)-O(11)	87.9(5)	O(102)-Ti(1)-O(11)	89.3(7)
Cl(11)-Ti(1)-O(21)	89.7(5)	Cl(12)-Ti(1)-O(21)	169.0(5)
O(102)-Ti(1)-O(21)	87.3(6)	O(11)-Ti(1)-O(21)	83.3(6)
Cl(12)-Ti(1)-O(31)	90.5(5)	Cl(11)-Ti(1)-O(31)	89.2(6)
O(11)-Ti(1)-O(31)	80.1(7)	O(102)-Ti(1)-O(31)	165.4(7)
O(21)-Ti(1)-O(31)	81.5(6)	Cl(21)-Ti(2)-Cl(22)	96.0(3)
Cl(21)-Ti(2)-O(102)	98.6(6)	Cl(22)-Ti(2)-O(102)	100.8(6)
Cl(21)-Ti(2)-O(12)	87.6(5)	Cl(22)-Ti(2)-O(12)	168.5(5)
O(102)-Ti(2)-O(12)	89.4(7)	Cl(21)-Ti(2)-O(22)	167.5(6)
Cl(22)-Ti(2)-O(22)	90.6(5)	O(102)-Ti(2)-O(22)	90.5(7)
O(12)-Ti(2)-O(22)	83.9(6)	Cl(21)-Ti(2)-O(41)	88.3(5)
Cl(22)-Ti(2)-O(41)	89.2(5)	O(102)-Ti(2)-O(41)	167.1(7)
O(12)-Ti(2)-O(41)	79.9(6)	O(22)-Ti(2)-O(41)	81.2(6)
Ti(1)-O(102)-Ti(2)	138.3(9)	Ti(1)-O(11)-C(11)	134.8(15)
Ti(2)-O(12)-C(11)	131.6(15)	O(11)-C(11)-O(12)	121.6(21)
Ti(1)-O(21)-C(21)	132.9(15)	Ti(2)-O(22)-C(21)	132.6(16)
O(21)-C(21)-O(22)	122.1(23)	Ti(1)-O(31)-C(31a)	151.3(20)
Ti(1)-O(31)-C(31b)	143.9(32)	O(31)-C(31a)-O(32a)	117.8(29)
O(31)-C(31b)-O(32b)	124.1(61)	Ti(2)-O(41)-C(41)	140.5(20)
O(41)-C(41)-O(42)	121.4(31)		

The compounds described here, $[\{TiCl_2(O_2CR)(RCO_2H)\}_2O]$ (R=Et, CMe_3), now demonstrate that in the absence of other donor ligands, the sixth position of the titanium octahedra can be occupied by carboxylic acid molecules. This particular feature is noteworthy since it is known that the reaction of carboxylic acids with $TiCl_4$ evolves HCl with the formation of $[TiCl_3(O_2CR)]$ (R=alkyl, aryl) species. Therefore compounds of the type $[\{TiCl_2(O_2CR)(RCO_2H)\}_2O]$ (R=Et, CMe_3) provide further unusual examples, in addition to the characterised titanium species $[Ti_2Cl_7(O_2CR)(RCO_2H)]$ (R=*p*-ClC_6H_4, CH=CHMe)[170] of compounds containing both a reactive Ti-Cl bond and a co-ordinated acid molecule at the same metal centre.

The constraints imposed by the two bridging carboxylate ligands cause the Ti-O-Ti unit to be bent, subtending an angle of 137.3 (R=Et) and 138.3° (R=CMe_3). This is comparable to the Ti-O-Ti angle (137.2°) of the analogous ethyl acetate adduct $[\{TiCl_2(O_2CPh)(MeCO_2Et)\}_2O]$. As a consequence of the deviation from the ideal 180°, naturally the two titanium atoms lie closer together, although Ti---Ti distances of 3.340 (R=Et) and 3.307Å (R=CMe_3) and also 3.31Å of the previously reported $[\{TiCl_2(O_2CPh)(MeCO_2Et)\}_2O]$ indicate that Ti---Ti bonding is not present.

The Ti---Ti distance is however, significantly shorter than those found for example in the tetrameric compound $[(\eta^5\text{-}C_5H_4Me)Ti(\mu_2\text{-}O)Cl]_4$ (3.53-3.58Å) whose Ti-O-Ti angles (of near 157°) are a typical example of the values found in titanium cyclopentadienyl derivatives containing a μ_2-O bridging group.[210] In this latter case, no other bridge apart from the μ_2-O is present and therefore the wider angle is most probably due to the lack of constraints arising from the absence of other bridging ligands. Further examples of large Ti-O-Ti angles occur in the titanium compounds $[Ti(acac)_2Cl]_2O$ (167.5°)[213] and $[Ti(CH_2Ph)_3]_2O$ (linear, 180°).[212]

The bridging carboxylate O-C-O angles of 123.6 (R=Et) and 121.9° (R=CMe_3) are only slightly larger than the ideal 120° for angles around a sp^2 hybridised carbon atom, therefore there is no apparent strain in the carboxylate bridging unit. This is also

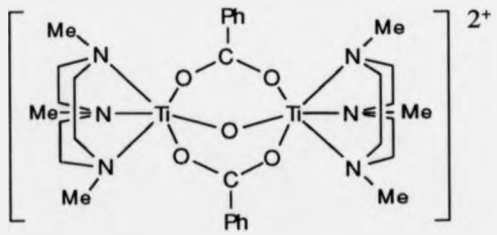
seen in $[\{TiCl_2(O_2CPh)MeCO_2Et\}_2O]$ where the O-C-O angle is 123.3°. It therefore appears that the μ_2-O bridge is the more flexible unit.

The average C-O-Ti angles of 133.1 (R=Et) and 133.0° (R=CMe_3) are somewhat larger than the ideal 120°. However, this still allows the formation of a stable six membered ring.

The average Ti-O_{oxo} bond distances are 1.794 (R=Et) and 1.769Å (R=CMe_3), which are very close to that found in $[\{TiCl_2(O_2CPh)MeCO_2Et\}_2O]$ of 1.783Å. The Ti-O distances are graduated as

Ti-O, *neutral acid ligand*		Ti-O, *acid anion*		Ti-O, *oxo bridge*
2.095Å (R=Et)	>	2.061Å (R=Et),	>	1.794Å (R=Et)
2.112Å (R=CMe_3)		2.049Å (R=CMe_3)		1.769Å (R=CMe_3)

thus indicating the relative strengths of the Ti-O bond and also the π character of the Ti-O-Ti bridge.



(2.12)

A titanium(III) compound $[Ti_2(\mu_2\text{-}O)(\mu_2\text{-}O_2CPh)_2L_2](PF_6)_2$ **(2.12)** (L=N,N',N''-trimethyl-1,4,7-triazacyclononane) contains the $[Ti_2(\mu_2\text{-}O)(\mu_2\text{-}O_2CR)_2]^{2+}$ core. It has a Ti-O-Ti angle of 122.7°, and a mean Ti-μ_2-O distance of 1.82Å, which is very short for the Ti^{III}-oxo bond.[207] The Ti-μ_2-O bonds have a strong *trans* influence on the *trans* Ti-N bonds, which are about 0.10Å longer than the corresponding *cis* Ti-N bonds. In addition, the Ti---Ti distance is 3.198Å which rules out direct Ti-Ti bonding.

The positioning of the co-ordinating acid ligand in the *trans* position of the species $[\{TiCl_2(O_2CEt)(EtCO_2H)\}_2O]$ and $[\{TiCl_2(O_2CCMe_3)(Me_3CCO_2H)\}_2O]$ may be due to the *trans* influence of the bridging oxygen. The *trans* influence is attributable

to the fact that two *trans* ligands will both depend on the participation of one metal orbital, and the more one ligand preempts this orbital, the weaker will be the bond to the other ligand. Thus, if a chlorine atom, being a stronger ligand than the neutral carboxylic acid, is in the *trans* position to the bridging oxygen, the μ_2-oxo bond will be longer, possibly putting a strain on the carboxylate bridge by opening further the O-C-O carboxylate angle and the C-O-Ti angles. This strain would be unfavourable and therefore correct accord would be kept by the carboxylic acid, as a weaker ligand, co-ordinating in this position.

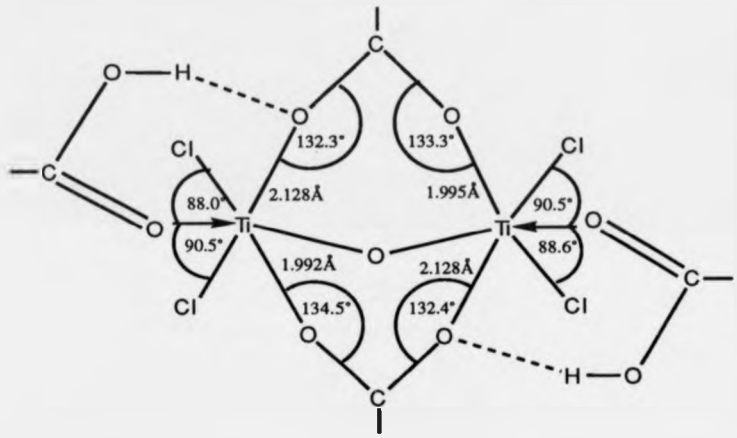


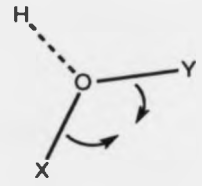
Figure 2.6 Structural Core of the compound $[\{TiCl_2(O_2CEt)(EtCO_2H)\}_2O]$ indicating the presence of hydrogen bonding in the molecule.

There is some apparent hydrogen bonding present in the species $[\{TiCl_2(O_2CR)(RCO_2H)\}_2O]$ (R=Et, CMe_3). In the case of the more disordered trimethylacetate derivative, the association is not very clear, but for the propanoate species, Figure 2.6 above, the carboxylate O-Ti bond lengths are slightly uneven and the hydrogen of the neutral co-ordinating acid shows some association with the oxygen of the bridging carboxylate group.

Due to the attraction of the proton of the co-ordinating acid, the oxygen involved with the association has a slightly lengthened $Ti\text{-}O_{carboxylate}$ bond. The deviation is only

slight but it is also seen in the Ti-O-C angles showing the more acute angle of the oxygen arising from it being 'pulled' away from its ideal position.

No H-bond interaction



Weak H-bond interaction
closes X-O-Y angle slightly

The mean Ti-Cl distances are 2.288 (R=Et) and 2.262Å (R=CMe_3) which are comparable to those found in [{$TiCl_2(O_2CPh)MeCO_2Et$}$_2$O] of 2.266Å. The Cl-Ti-Cl angles have opened up to 97.1 (R=Et) and 96.9° (R=CMe_3) from the ideal 90° but the mean Cl-Ti-O_{ligand} bond angles are 89.4 (R=Et) and 89.3° (R=CMe_3). It can be seen more clearly from the propanoate core, Figure 2.6 on the previous page, that the Cl-Ti-O_{ligand} angles are slightly uneven due to slight closing in on one side because of the hydrogen bonding which occurs with the ligand hydroxyl group.

2.4.6. Preparation of the compound $[Ti_2OCl_3(O_2CEt)_3(EtCO_2H)]$

It has been discussed that the compound $[\{TiCl_2(O_2CEt)(EtCO_2H)\}_2O]$ may be prepared by the addition of $TiCl_4$ to a solution of propanoic acid in a 1:2.5 molar ratio at ambient temperature. Further to this, another product may be isolated which is best formulated as $[Ti_2OCl_3(O_2CEt)_3(EtCO_2H)]$. Thus the addition of $TiCl_4$ (1 mol) to a solution of propanoic acid (2.5 mol) in light petroleum at room temperature produces a yellow oily precipitate which on stirring for 4 days converts to a white powder. Elemental analysis is consistent with the title formulation and it is proposed that the product occurs according to the equation below.

$$2TiCl_4 + 5EtCO_2H \longrightarrow [Ti_2OCl_3(O_2CEt)_3(EtCO_2H)] + EtCOCl + 4HCl$$

The equation is corroborated by the presence of propanoyl chloride in the mother liquor which was identified by IR spectroscopy. It is envisaged that the reaction occurs *via* the product $[\{TiCl_2(O_2CEt)(EtCO_2H)\}_2O]$ as isolation of the solid after 2 days and subsequent IR analysis indicates a mixture of both the latter product and $[Ti_2OCl_3(O_2CEt)_3(EtCO_2H)]$.

$$2TiCl_4 + 5EtCO_2H \longrightarrow [\{TiCl_2(O_2CEt)(EtCO_2H)\}_2O] + EtCOCl + 3HCl$$

$$[\{TiCl_2(O_2CEt)(EtCO_2H)\}_2O] \longrightarrow [Ti_2OCl_3(O_2CEt)_3(EtCO_2H)] + HCl$$

In addition to elemental analysis, $[Ti_2OCl_3(O_2CEt)_3(EtCO_2H)]$ was further characterised by IR and ^1H NMR spectroscopy.

IR Spectrum of the compound $[Ti_2OCl_3(O_2CEt)_3(EtCO_2H)]$

Although formulated as a species containing a co-ordinated acid ligand, the IR spectrum of the title compound shows no indication of the hydroxyl moiety. In comparison, the compound $[\{TiCl_2(O_2CEt)(EtCO_2H)\}_2O]$ which also contains neutral propanoic acid ligands exhibits a broad hydroxyl stretching band at $3200cm^{-1}$. It is possible that this absorption band in the spectrum of the title compound is very broad and

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The equation is corroborated by the presence of propanoyl chloride in the mother liquor which was identified by IR spectroscopy. It is envisaged that the reaction occurs *via* the product $[\{TiCl_2(O_2CEt)(EtCO_2H)\}_2O]$ as isolation of the solid after 2 days and subsequent IR analysis indicates a mixture of both the latter product and $[Ti_2OCl_3(O_2CEt)_3(EtCO_2H)]$.

$$2TiCl_4 + 5EtCO_2H \longrightarrow [\{TiCl_2(O_2CEt)(EtCO_2H)\}_2O] + EtCOCl + 3HCl$$

$$[\{TiCl_2(O_2CEt)(EtCO_2H)\}_2O] \longrightarrow [Ti_2OCl_3(O_2CEt)_3(EtCO_2H)] + HCl$$

In addition to elemental analysis, $[Ti_2OCl_3(O_2CEt)_3(EtCO_2H)]$ was further characterised by IR and ^1H NMR spectroscopy.

IR Spectrum of the compound $[Ti_2OCl_3(O_2CEt)_3(EtCO_2H)]$

Although formulated as a species containing a co-ordinated acid ligand, the IR spectrum of the title compound shows no indication of the hydroxyl moiety. In comparison, the compound $[\{TiCl_2(O_2CEt)(EtCO_2H)\}_2O]$ which also contains neutral propanoic acid ligands exhibits a broad hydroxyl stretching band at $3200cm^{-1}$. It is possible that this absorption band in the spectrum of the title compound is very broad and

goes undetected. However, this is in contrast to the ^1H NMR spectrum where the hydroxyl proton may be observed for both compounds.

The υ(C=O) of the co-ordinated acid may be assigned to a strong absorption band at 1608cm^{-1} which is indicative of the co-ordination of the acid carbonyl oxygen to the titanium metal centre in the title compound. Further, the value of 1608cm^{-1} is in accord with that found for the compound $[Ti_2Cl_7(O_2CEt)(EtCO_2H)]$ for which υ(C=O) has been assigned at 1601cm^{-1}. The carboxylate stretching bands $\upsilon(COO)_{asym}$ and $\upsilon(COO)_{sym}$ are assigned to absorption bands at 1520 and 1397cm^{-1} respectively, which gives a Δ value of 123cm^{-1}. This is consistent with the presence of bidentate chelating or bridging carboxylate groups. The analogous values for $[\{TiCl_2(O_2CEt)(EtCO_2H)\}_2O]$ are 1520 and 1405cm^{-1} for $\upsilon(COO)_{asym}$ and $\upsilon(COO)_{sym}$ respectively, indicating that Δ=115cm^{-1}. X-ray structure determination of this latter compound has revealed that the propanoate ligands are in a symmetrically bridging co-ordination mode. Due to the similarity of these carboxylate stretching frequencies with those of the title compound it may therefore be tentatively assumed that bridging carboxylate ligands are also present in $[Ti_2OCl_3(O_2CEt)_3(EtCO_2H)]$.

The υ(Ti-O-Ti) may be assigned to an absorption band at 684cm^{-1}. This latter band is not as broad as that found for the analogous stretching signal in the IR spectrum of the species $[\{TiCl_2(O_2CR)(RCO_2H)\}_2O]$ (R=Me, Et, CMe_3) possibly indicating that a weaker μ_2-O bridge or possibly a μ_3-O bridge exists in the title compound.

Bands attributable to υ(Ti-Cl) of the terminal chlorine atoms are assigned at 446, 400 and 350cm^{-1}.

^1H NMR Spectrum of $[Ti_2OCl_3(O_2CEt)_3(EtCO_2H)]$

The ^1H NMR spectrum of the title compound in $CDCl_3$ shows broad multiplets situated at δ2.8-2.25 and 1.5-1.0 which are attributable to both the propanoate ligand protons and the co-ordinating acid protons. A broad signal centred at δ8.45 is assigned to the hydroxyl proton of the co-ordinated acid.

2.4.7 A Possible Structure and Route to $[Ti_2OCl_3(O_2CEt)_3(EtCO_2H)]$

It appears very likely that the formation of the title compound occurs *via* the formation of the species $[\{TiCl_2(O_2CEt)(EtCO_2H)\}_2O]$ as both products have been detected in the product of the reaction at different stages. Thus after 5 hours stirring, $[\{TiCl_2(O_2CEt)(EtCO_2H)\}_2O]$ may be isolated, and after 4 days the product is $[Ti_2OCl_3(O_2CEt)_3(EtCO_2H)]$. However, after 2 days both compounds may be observed in the IR spectrum of the solid product. The IR spectra of the product of the addition of $TiCl_4$ (1 mol) to propanoic acid (2.5 mol) at room temperature in hexane solution after 5 hours, 2 days and 4 days are shown in Figure 2.7.

It has been previously reported by Amaudrut and co-workers that the reaction of $TiCl_4$ with popanoic acid in a 1:2 ratio gave two possible compounds.[175] These were labelled α and β bis-propanoate, as the structure of neither species was able to be unequivocally established. The α compound was formulated as $[TiCl_2(O_2CEt)_2]$ but in light of the reactions carried out for this thesis with subsequent X-ray investigation, it is apparent that the α compound was misformulated and actually should be formulated as $[\{TiCl_2(O_2CEt)(EtCO_2H)\}_2O]$. The IR spectra of Amaudrut's α and β forms which have been published, are identical to those of $[\{TiCl_2(O_2CEt)(EtCO_2H)\}_2O]$ and $[Ti_2OCl_3(O_2CEt)_3(EtCO_2H)]$ respectively which have been isolated here.

It is now believed that after 5 hours, the following reaction has occurred.

$$2TiCl_4 + 5EtCO_2H \longrightarrow [\{TiCl_2(O_2CEt)(EtCO_2H)\}_2O] + EtCOCl + 3HCl$$

And then after 4 days, a further mole of HCl is eliminated, thus,

$$[\{TiCl_2(O_2CEt)(EtCO_2H)\}_2O] \longrightarrow [Ti_2OCl_3(O_2CEt)_3(EtCO_2H)] + HCl$$

However, studies have revealed that isolation of the compound $[\{TiCl_2(O_2CEt)(EtCO_2H)\}_2O]$ with subsequent redissolving in dichloromethane and stirring for 3 days, does not give $[\{Ti_2OCl_3(O_2CEt)_3(EtCO_2H)]$ and the former compound is isolated unchanged from solution.

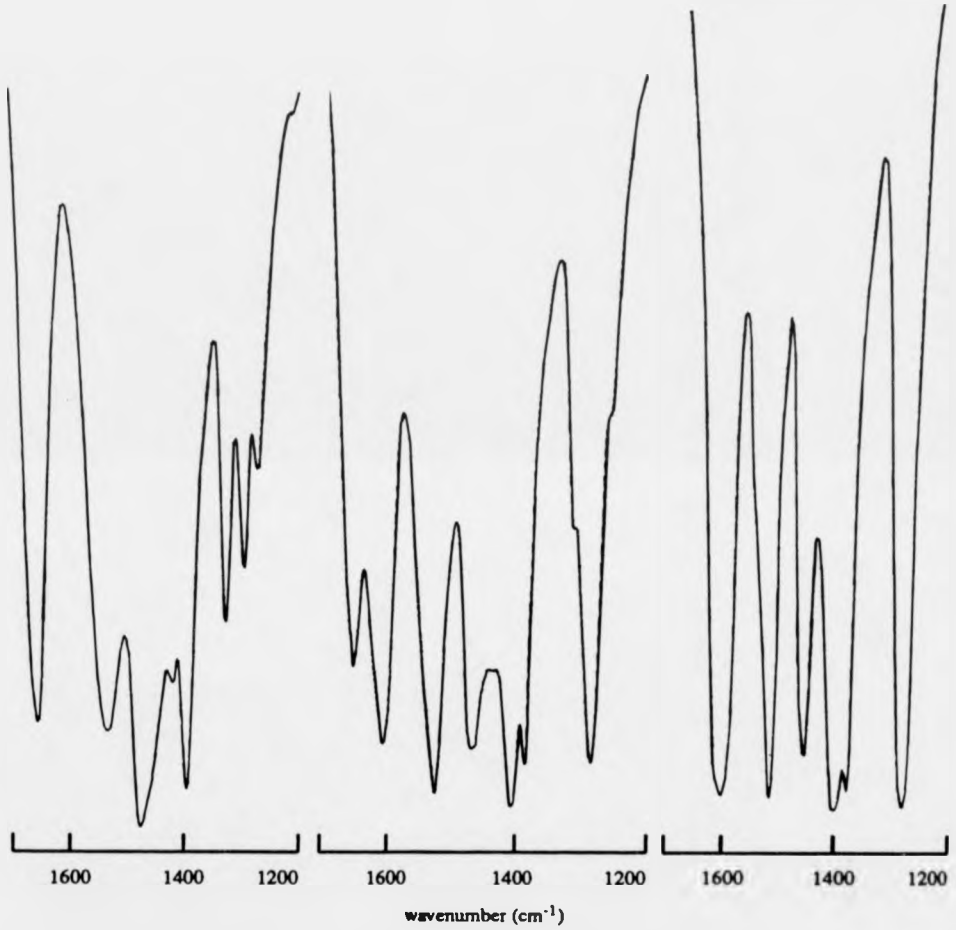


Figure 2.7 IR spectra of the product of the reaction of $TiCl_4$ with propanoic acid (ratio 1:2.5) after 5 hours, 2 days and 4 days.

Heating $[\{TiCl_2(O_2CEt)(EtCO_2H)\}_2O]$ in a bid to eliminate a mole of HCl produces the compound $[Ti_3O_2Cl_3(O_2CEt)_5]$ which will be discussed in greater detail in Chapter 4. The reaction is proposed to occur according to the following route.

$$3[\{TiCl_2(O_2CEt)(EtCO_2H)\}_2O] \xrightarrow{70°C} 2[Ti_3O_2Cl_3(O_2CEt)_5] + EtCO_2H + EtCOCl + 5HCl$$

In comparison, isolation of $[Ti_2OCl_3(O_2CEt)_3(EtCO_2H)]$ with subsequent refluxing in chloroform (~70°C) has also produced the species $[Ti_3O_2Cl_3(O_2CEt)_5]$, thus the reaction could possibly be

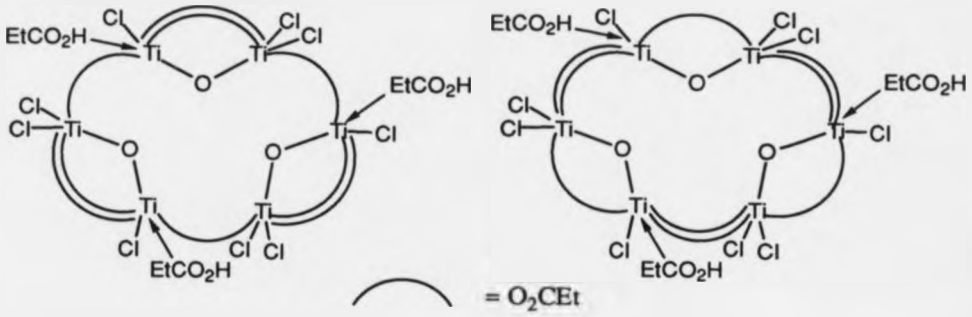
$$3[Ti_2OCl_3(O_2CEt)_3(EtCO_2H)] \xrightarrow{70°C} 2[Ti_3O_2Cl_3(O_2CEt)_5] + EtCO_2H + EtCOCl + 2HCl$$

It therefore seems likely that on heating, the conversion of $[\{TiCl_2(O_2CEt)(EtCO_2H)\}_2O]$ to $[Ti_3O_2Cl_3(O_2CEt)_5]$ occurs *via* the formation of $[Ti_2OCl_3(O_2CEt)_3(EtCO_2H)]$.

The solubilities of the compounds $[\{TiCl_2(O_2CEt)(EtCO_2H)\}_2O]$ and $[Ti_2OCl_3(O_2CEt)_3(EtCO_2H)]$ differ considerably; the former species being readily soluble in CH_2Cl_2, $CHCl_3$ and toluene while the latter is only partially soluble. This factor may indicate a greater association of the species $[Ti_2OCl_3(O_2CEt)_3(EtCO_2H)]$. Thus on heating $[\{TiCl_2(O_2CEt)(EtCO_2H)\}_2O]$ the elimination of HCl may facilitate the formation of a hexanuclear species which then undergoes a series of reactions and cleaves into two fragments, which may be represented as

$$3[\{TiCl_2(O_2CEt)(EtCO_2H)\}_2O] \longrightarrow [Ti_6O_3Cl_9(O_2CEt)_9(EtCO_2H)_3] \longrightarrow 2[Ti_3O_2Cl_3(O_2CEt)_5]$$

From the results gained it is possible to formulate likely structures for the compound $[Ti_2OCl_3(O_2CEt)_3(EtCO_2H)]$. No suitable binuclear species may be formulated, but tetranuclear, hexanuclear, and oligomeric species may be postulated. Thus two possible structures **(2.13)** and **(2.14)** may be envisaged.



(2.13) (2.14)

CHAPTER THREE

THE REACTIONS OF THE COMPOUNDS $[\{TiCl_2(O_2CR)(RCO_2H)\}_2O]$ (R=Me, Et, CMe_3) AND $[\{TiCl_2(O_2CH_2OC_6F_5)\}_2O]$ WITH TETRAHYDROFURAN

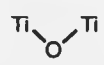
3. INTRODUCTION

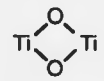
Some of the titanium compounds discussed in the previous chapter contain an oxide ligand. A variety of titanium oxo compounds have been characterised and some of these will now be mentioned in relation to their Ti-O frameworks. In addition, the reactions of titanium carboxylates with various ligands such as water will be discussed.

3.1. Titanium(IV) μ_2-Oxo Species

It is known that μ_2-oxo linkages predominate in the oxo compounds of titanium giving Ti-O-Ti units.[196] The double oxo bridged species $[Ti\text{-}(\mu_2\text{-}O)_2\text{-}Ti]^{4+}$ is very rarely encountered, but for μ_2-O bridging species three bridging modes have been identified for linkages between two titanium metal atoms as shown below.

a) Ti—O—Ti linear

b)  bent

c)  double oxygen bridge

A single oxo bridge, μ_2-O, may subtend an angle varying between 135-180°, the angle being determined by steric or electronic factors. This is seen in the compounds discussed in Chapter 2, namely $[\{TiCl_2(O_2CR)(RCO_2H)\}_2O]$ (R=Et, CMe_3) where the oxo bridge is supported by two carboxylate ligands and the bridging oxygen subtends an angle of 137.3° (R=Et) and 138.3° (R=CMe_3) to accommodate this unit. As well as the dinuclear 'linear' species, oxo bridges may be involved in cyclic entities, as with the tetranuclear frameworks of $[\{CpTiClO\}_4]$[213] and $[\{Cp^*TiBrO\}_4]$.[214]

The largest group of titanium oxo complexes are those containing cyclopentadienyl ligands. Compounds of the general formula $[(Cp_2TiX)_2(\mu_2\text{-}O)]$ (where X=Cl, Br) have near linear M-O-M bridges and staggered $[Cp_2MX]$ groups. This conformation allows maximum overlap of the single empty orbital of each of the $[Cp_2MX]$ fragments with a lone

pair of electrons on the oxygen. Non-cyclopentadienyl containing titanium oxo species are of lesser numbers but due to their relevance in this thesis, these will now be briefly discussed.

3.2. Non-Cyclopentadienyl Containing μ_2-Oxo Titanium Compounds

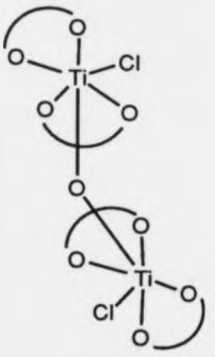
Unsupported binuclear μ_2-O bridging compounds are the most common titanium oxo species. A small selection of non-cyclopentadienyl containing μ_2-O compounds is shown in Table 3.1, which serves to illustrate the variety of Ti-O-Ti angles which may be found for these species. The majority of these compounds are prepared by controlled hydrolysis reactions.

Table 3.1 Some non-cyclopentadienyl containing binuclear oxo titanium compounds.

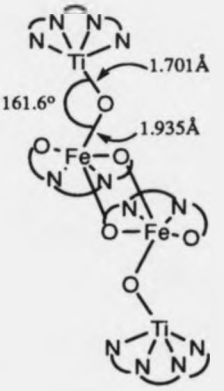
Compound	Average Ti-μ-O (Å)	Ti-O-Ti angle (°)	Ref.
$[\{Ti(CH_2C_6H_5)_3\}_2O]$	1.798	180	212
$[\{Ti(acac)_2Cl\}_2O]$ **(3.1)**	1.80	167.5	211
$[\{Ti(N_2{}^tBu_2SPh)Cl_2\}_2O]$	1.784	178.2	215
$[\{Ti(TACH)\}_2O]$	1.838	152	216
$[\{TiCl_4(MeCN)\}_2O][PPh_4]_2$	1.804	180	217
$[\{TiCl((OC_6H_4CHN)_2C_6H_{11})\}_2O]$	1.806	168.3	218
TACH = the triimido ion of 1,5,9,13 tetra-azacyclohexadecane, $N_4C_{12}H_{25}$			

The structure of μ_2-oxo-bis-chloro-bis-acetonato-titanium(IV) chloroform solvate **(3.1)** has been determined by X-ray diffraction and is made up of two $[TiCl(C_5H_7O_2)_2]$ units joined by an oxygen atom.[211] The acetylacetonate groups are *cis* to each other.

Heterobimetallic μ_2-oxo species with titanium are few in number. Goedken and Young reported the crystal structure of the compound $[\{(C_{22}H_{22}N_4)Ti\text{-}O\text{-}Fe(salen)\}_2][BPh_4]_2$ **(3.2)** which contains two Ti-O-Fe bridges.[219]

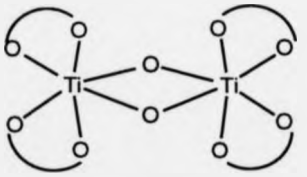


(3.1)



(3.2)

The Ti-O-Fe stretching vibration was reported to occur in the IR at 866cm^{-1}. A further example of a heterobimetallic species has been prepared by Floriani and co-workers.[220] In this case the oxygen bridges a titanium and a vanadium atom. The angle at the bridging oxygen in [Cl(acacen)V-O-$TiCl_3(THF)_2$](THF) is 169.1° with Ti-O 1.691Å and V-O 1.973Å.



Average dimensions

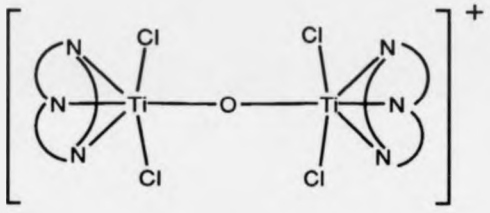
Ti-O-Ti	96.6°
O-Ti-O	83.4°
Ti-(μ-O)	1.828Å
Ti----Ti	2.729Å
O----O	2.430Å

(3.3)

Smith *et al* determined the crystal structure of [{$Ti(acac)_2(\mu_2\text{-}O)$}$_2$] **(3.3)** and the bis-dioxane adduct [{$Ti(acac)_2(\mu_2\text{-}O)$}$_2$].$2C_4H_8O_2$.[221] Both compounds contained a di-μ_2-oxo titanium unit which is rare in titanium oxo species. The titanium atoms are in an octahedral environment with the di-μ_2-oxo di-titanium unit planar and slightly distorted from a square. As can be seen by comparison with the single μ_2-O species, the Ti-O-Ti angle has closed up to 96.6° due to the constraints of a further μ_2-O bridge being present. This reduction in the angle causes the Ti---Ti distance to be reduced to 2.729Å compared to those in the compounds [{$TiCl_2(O_2CR)(RCO_2H)$}$_2$O] (R=Et, CMe_3) which have metal-metal

distances of 3.340 (R=Et) and 3.307Å ($R=CMe_3$) due to the presence of bridging carboxylate ligands which lessen the restriction of the Ti-O-Ti bridge.

Complexes containing the $[Ti^{III}\text{-}O\text{-}Ti^{IV}]^{5+}$ core are very rare, and to date only one mixed valence species has been structurally characterised. The compound $[\{L_2Ti_2Cl_4(\mu\text{-}O)\}Cl.2H_2O]$ **(3.4)** (L=1,4,7-trimethyl-1,4,7-triazacyclononane) was obtained from a solution of $TiCl_3$ in dry dimethylformamide to which an equimolar amount of the ligand L was added under an argon atmosphere at 90°C with the addition of a few drops of water and a small volume of air while the solution was still hot.[222] Subsequent cooling to 0°C produced dark blue crystals of the mixed valence species.



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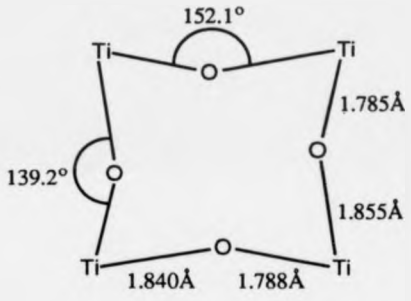


(3.5)

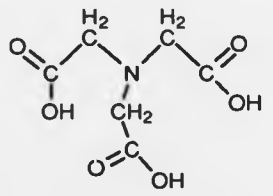
The magnetic moment of this species is 1.72BM, clearly containing one unpaired electron per binuclear unit. The Ti-O-Ti moiety is linear and the two titanium atoms are equivalent. The $Ti\text{-}O_{oxo}$ distance at 1.872Å is quite short, indicating some considerable double-bond character. However, it is significantly longer than the $Ti\text{-}O_{oxo}$ distances in its organometallic counterparts such as $[(CpTiCl_2)_2(\mu_2\text{-}O)]$ (1.777Å).[223]

As mentioned previously, μ_2-oxo bridges may be involved in cyclic structures. The molecular structure of ammonium titanyl oxalate monohydrate $[NH_4]_2[TiO(C_2O_4)_2].H_2O$ was determined by X-ray diffraction and was found to be composed of an eight membered ring of alternating titanium and oxygen atoms.[224] The Ti-O framework of the tetramer **(3.5)** is shown above, illustrating the deviation from a perfect square of the Ti_4O_4 core. There are two oxalate anions chelating in a bidentate fashion to each titanium atom to give

each metal atom the expected co-ordination number of six. Again, as with many species of this type, the Ti-O_{oxo} distances in the ring are short, suggesting a fair amount of dπ-pπ bonding.

A similar compound $Cs_4[\{Ti(NTA)O\}_4].6H_2O$ [NTA=nitrilotriacetic acid **(3.6)**] has been prepared and fully characterised by Wieghardt and co-workers.[225] The X-ray structure analysis of the caesium salt reveals the presence of the tetrameric anions $[\{Ti(NTA)O\}_4]^{4-}$. The titanium(IV) centres are six co-ordinate and the μ_2-oxo bridges are not symmetric. A short (~1.74Å) and a longer Ti-O bond (~1.90Å) alternate, forming a puckered eight-membered ring with the Ti-O-Ti bond angles ranging from 148.8-169.8°.

Recently a heterometallic cyclic species of molecular formula $[\{(TiCl_2)(\mu_2\text{-}O)_2(Si^tBu_2)\}_2]$ **(3.7)** has been structurally characterised.[226] The molecule has an average Ti-O_{oxo} distance of 1.747Å with Ti-O-Si angles of 156.0 and 169.1° and an O-Ti-O angle of 107.9°.



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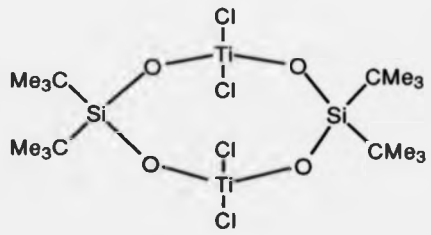


(3.7)

3.3. Cyclopentadienyl Titanium Oxo Species

Many studies concerning cyclopentadienyl titanium oxo species have been carried out and information concerning these species may be obtained from many detailed reviews on the subject.[8] Most of this type of oxo species have been produced by controlled hydrolysis reactions. Some of these will now be briefly reviewed.

The simplest organometallic oxo species are composed of two titanium centres linked by an oxygen atom. Some of these examples are shown in Table 3.2.

Table 3.2 Some dinuclear species containing the $Ti_2(\mu_2\text{-}O)$ unit.

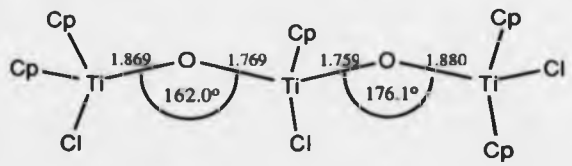
Compound	Ti-O-Ti (°)	$Ti\text{-}O_{oxo}$ (Å)	Ref.
$[(Cp_2TiCl)_2O]$	173.81	1.837	227
$[(CpTiCl_2)_2O]$	180	1.777	223
$[Cp^*TiMe_2][Cp^*TiMe(\eta^2\text{-}MeNNCPh_2)](\mu\text{-}O)$	161.9	1.861 and 1.788	228
$[\{Cp_2Ti(NO_3)\}_2O]$	171.8	1.835	229

Examples of dinuclear species containing the $Ti_2(\mu_2\text{-}O)_2$ unit are very rare. Titanium-oxygen measurements for two of these species are shown in Table 3.3.

Table 3.3 Titanium-oxygen measurements for species containing the $Ti_2(\mu_2\text{-}O)_2$ core.

Compound	Ti-O-Ti (°)	O-Ti-O (°)	$Ti\text{-}O_{oxo}$ (Å)	Ref.
$[(Cp^*Ti)_2(\mu\text{-}O)_2(\mu\text{-}\eta^5\text{:}\eta^1\text{-}C_5(Me)_4CH_2)]$	93.1	79.9	1.961, 1.787	230
$[\{(\eta^5\text{-}C_5H_2(SiMe_3)_3\text{-}1,2,4)Ti(\mu\text{-}O)Cl\}_2]$	95.78	84.23	1.814, 1.835	231

Trinuclear species are not generally linear, but a rare example is $[\{Cp_2TiCl\}_2\{CpTiCl\}(\mu_2\text{-}O)_2]$ **(3.8)** which has been characterised by X-ray diffraction.[232]



(3.8)

Other trimeric compounds involve $Ti_3(\mu_3\text{-}O)$ species such as $[\{CpTi(OMe)(\mu_2\text{-}OMe)\}_3(\mu_3\text{-}O)]^+$ [233] and $[\{CpTi(\mu_2\text{-}OH)(\mu_2\text{-}OOCH)\}_3(\mu_3\text{-}O)]^+$,[234] but generally cyclic derivatives of alternating titanium-oxygen atoms are the most common containing a $Ti_3(\mu_2\text{-}O)_3$ core as displayed in Table 3.4.

Table 3.4 Titanium-oxygen measurements for some compounds containing the $Ti_3(\mu_2\text{-}O)_3$ core.

Compound	Mean Ti-O_{oxo} (Å)	Ti-O-Ti (°)	O-Ti-O (°)	Ref.
$[\{Cp^*TiMeO\}_3]$	1.823	104.8-106.0	131.6-133.5	235
$[\{Cp^*TiBrO\}_3]$	1.819	102.7-104.1	132.4-135.6	236
$[\{Cp^*TiClO\}_3]$	1.823	102.9-103.9	131.4-135.3	237

Tetranuclear species have also been found to have a cyclic structure forming an eight membered ring with a $Ti_4(\mu_2\text{-}O)_4$ core. Such examples are $[\{(C_5HMe_4)Ti(\mu_2\text{-}O)Br\}_4]$,[236] $[\{(\eta^5\text{-}C_5H_4(SiMe_3))Ti(\mu_2\text{-}O)(NCS)\}_4]$[237] and $[\{CpTi(\mu_2\text{-}O)(OC_9H_{11})\}_4]$.[238]

$Ti_4(\mu_2\text{-}O)_5$ and $Ti_4(\mu_2\text{-}O)_6$ derivatives may be prepared by using carefully controlled hydrolysis conditions. The resultant compounds are not planar and consist of cages made up of titanium and oxygen atoms. Examples of these compounds are $[(Cp^*Ti)_4(\mu_2\text{-}O)_5Cl_2]$[239] and $[(Cp^*Ti)_4(\mu_2\text{-}O)_6]$.[240]

In addition to the compounds which have been mentioned a number of species containing μ_3-O groups are known, namely $[(Cp'Ti)_6(\mu_3\text{-}Cl)_4(\mu_3\text{-}O)_4]$ ($Cp'=C_5H_4Me$), $[(CpTi)_6(\mu_3\text{-}Cl)_2(\mu_3\text{-}O)_6]$[241] and $[(CpTi)_6(\mu_3\text{-}O)_8]$[242] which again have a cage type structure.

3.4. Acceptor Properties of Titanium(IV) Carboxylates

The acceptor properties of titanium(IV) carboxylates with some neutral ligands have been studied. No structural characterisations of these addition compounds by X-ray diffraction have been reported, and therefore any prediction concerning the arrangement of the ligands around the metal centre is tentative. As structural data of the initial titanium(IV) carboxylates is also limited, this adds to the uncertainty of the type of product formed.

Nitrosyl chloride (NOCl) reacts with the titanium(IV) carboxylates $[TiCl_3(O_2CR)]$ (R=Me, Et, ^{n}Pr, ^{i}Pr, ^{t}Bu) to give a mixture of both the $TiCl_4$ adduct and a titanium(IV) bis-

carboxylate which were identified by their X-ray powder diffraction data.[243] The reaction pathway is proposed to follow the equation below.

$$2[TiCl_3(O_2CR)] + 2NOCl \longrightarrow [TiCl_4.2NOCl] + [TiCl_2(O_2CR)_2]$$

With acetonitrile, it was found that the action of one mole of MeCN on one mole of the titanium monocarboxylate proceeded in a similar fashion to give the adduct $[TiCl_4.2MeCN]$ and the biscarboxylate $[TiCl_2(O_2CR)_2]$.[244]

Reaction of acetyl chloride, MeCOCl, with either $[TiCl_3(O_2CMe)]$ or $TiOCl_2$ produces the compound $[TiCl_3(O_2CMe)(MeCOCl)]$.[245] The co-ordinated acid chloride carbonyl stretching band is seen in the IR spectrum of the product at $1750cm^{-1}$. This is in line with the carbonyl stretching frequency of the co-ordinated acetyl chloride in the adduct $[TiCl_4.MeCOCl]$ where the absorption band is found at $1760cm^{-1}$.[246] On heating $[TiCl_3(O_2CMe)(MeCOCl)]$ at 65°C under reduced pressure $[TiCl_3(O_2CMe)]$ was produced.

The action of excess $POCl_3$ on compounds of the type $[TiCl_3(O_2CR)]$ (R=Me, Et, Pr, ^{i}Pr, ^{t}Bu) has been studied.[247] Information gained from the IR spectra of the reaction liquors indicated that the initial reaction produced the adduct $[TiCl_4.POCl_3]$ and the carboxylate $[TiCl_2(O_2CR)_2]$. After some hours, the formation of acid chloride was noted in the reaction liquors and a product of the stoichiometry $[TiOCl_2.2POCl_3]$ was isolated.

If excess $POCl_3$ is allowed to react with $[TiCl_2(O_2CR)_2]$ (R=Me, Et, CH_2Cl, $CHCl_2$, ^{t}Bu) then the following reaction is proposed to occur.

$$[TiCl_2(O_2CR)_2] + 2POCl_3 \longrightarrow [TiO_2.2POCl_3] + 2RCOCl$$

The same product may be produced by decomposition of $[TiOCl_2.2POCl_3]$ by the following equation.

$$2[TiOCl_2.2POCl_3] \xrightarrow{110^oC} [TiO_2.2POCl_3] + [TiCl_4.2POCl_3]$$

Kapoor *et al* investigated the reactions of the carboxylates $[TiCl_3(O_2CR)]$ and $[TiCl_2(O_2CR)_2]$ with pyridine and showed that the metal atom in these compounds retains its Lewis acid character.[174] Whether the 1:1 or 1:2 adduct is formed depends upon the size of

carboxylate which were identified by their X-ray powder diffraction data.[243] The reaction pathway is proposed to follow the equation below.

$$2[TiCl_3(O_2CR)] + 2NOCl \longrightarrow [TiCl_4.2NOCl] + [TiCl_2(O_2CR)_2]$$

With acetonitrile, it was found that the action of one mole of MeCN on one mole of the titanium monocarboxylate proceeded in a similar fashion to give the adduct $[TiCl_4.2MeCN]$ and the biscarboxylate $[TiCl_2(O_2CR)_2]$.[244]

Reaction of acetyl chloride, MeCOCl, with either $[TiCl_3(O_2CMe)]$ or $TiOCl_2$ produces the compound $[TiCl_3(O_2CMe)(MeCOCl)]$.[245] The co-ordinated acid chloride carbonyl stretching band is seen in the IR spectrum of the product at $1750cm^{-1}$. This is in line with the carbonyl stretching frequency of the co-ordinated acetyl chloride in the adduct $[TiCl_4.MeCOCl]$ where the absorption band is found at $1760cm^{-1}$.[246] On heating $[TiCl_3(O_2CMe)(MeCOCl)]$ at 65°C under reduced pressure $[TiCl_3(O_2CMe)]$ was produced.

The action of excess $POCl_3$ on compounds of the type $[TiCl_3(O_2CR)]$ (R=Me, Et, Pr, ^{i}Pr, ^{t}Bu) has been studied.[247] Information gained from the IR spectra of the reaction liquors indicated that the initial reaction produced the adduct $[TiCl_4.POCl_3]$ and the carboxylate $[TiCl_2(O_2CR)_2]$. After some hours, the formation of acid chloride was noted in the reaction liquors and a product of the stoichiometry $[TiOCl_2.2POCl_3]$ was isolated.

If excess $POCl_3$ is allowed to react with $[TiCl_2(O_2CR)_2]$ (R=Me, Et, CH_2Cl, $CHCl_2$, ^{t}Bu) then the following reaction is proposed to occur.

$$[TiCl_2(O_2CR)_2] + 2POCl_3 \longrightarrow [TiO_2.2POCl_3] + 2RCOCl$$

The same product may be produced by decomposition of $[TiOCl_2.2POCl_3]$ by the following equation.

$$2[TiOCl_2.2POCl_3] \xrightarrow{110°C} [TiO_2.2POCl_3] + [TiCl_4.2POCl_3]$$

Kapoor *et al* investigated the reactions of the carboxylates $[TiCl_3(O_2CR)]$ and $[TiCl_2(O_2CR)_2]$ with pyridine and showed that the metal atom in these compounds retains its Lewis acid character.[174] Whether the 1:1 or 1:2 adduct is formed depends upon the size of

the carboxylate alkyl group. Therefore with R=Me, CH_2Cl, $CHCl_2$, CCl_3 the 1:2 adduct is formed. However, if R=Et, Pr, Bu, Pentyl the 1:1 adduct is produced. The products were characterised by elemental analysis. In agreement with this observation, adducts of the stoichiometry 1:2 are observed in the reaction of $[TiCl_2(O_2CH)_2]$ with pyridine, γ-picoline and quinoline.[178]

The Lewis acid character of compounds of the type $[Ti(O_2CR)_4]$ ($R=CH_2Cl$, $CHCl_2$, and CCl_3) with pyridine has been investigated, and are reported to give adducts of the formula $[Ti(O_2CR)_4.2C_5H_5N]$ which have been characterised by IR spectra and elemental analysis.[183,184,185]

3.5. Reactions of Titanium(IV) Tris(chloro)monocarboxylates of the General Formula $[TiCl_3(O_2CR)]$

Previous research from these laboratories has shown that partial hydrolysis of $[TiCl_3(O_2CPh)]$ in ethyl acetate, or tetrahydrofuran, yields the oxo derivatives $[\{TiCl_2(O_2CPh)L\}_2O]$ (L=$MeCO_2Et$ or THF) with the evolution of HCl, as shown by the equation below.[193]

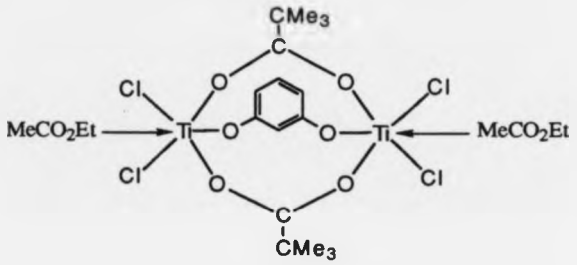
$$2[TiCl_3(O_2CPh)] + 2MeCO_2Et + H_2O \longrightarrow [\{TiCl_2(O_2CPh)(MeCO_2Et)\}_2O] + 2HCl$$

While this appears to be a general reaction for compounds of the type $[TiCl_3(O_2CR)]$ the yield of isolable oxo compound varies, but is generally low (~20% based on titanium), possibly due to the formation of other oxo species in the hydrolysis reaction.

Reactions with other ligands containing protic hydrogens likewise involve the evolution of hydrogen chloride.[170] Thus when the trimethylacetate derivative $[TiCl_3(O_2CCMe_3)]$ is treated with phenol in a 2:1 molar ratio in tetrahydrofuran the product analyses as the mixed carboxylate-phenoxide $[\{TiCl_2(O_2CCMe_3)THF\}_2(OPh)]$. The orange product is obtained in low yield, and its IR spectrum shows carboxylate absorption bands attributable to $\upsilon(COO)_{asym}$ and $\upsilon(COO)_{sym}$ at 1540 and 1430cm^{-1} respectively giving

a Δ value of 110cm^{-1}, thus indicating the presence of symmetrically bridging or chelating carboxylate ligands.

The product with resorcinol [1,3-$(HO)_2C_6H_4$], in ethyl acetate, is the dark red solid [{$TiCl_2(O_2CCMe_3)(MeCO_2Et)$}$_2(O_2C_6H_4)$]. Bands from $\upsilon(COO)_{asym}$ and $\upsilon(COO)_{sym}$ appear at 1650 and 1540cm^{-1} respectively giving a Δ value of 110cm^{-1}, which again implies the presence of bridging or chelating carboxylate ligands. One possible structure for this species is based on the structure of the hydrolysis product [{$TiCl_2(O_2CPh)(MeCO_2Et)$}$_2$O] and is shown below **(3.9)**.



(3.9)

Acetylacetone, $(MeCO)_2CH_2$, yields either [$TiCl_2(O_2CCMe_3)${$(MeCO)_2CH$}] or [$TiCl_2${$(MeCO)_2CH$}$_2$] with 1 and 2 moles of the ligand respectively,[170,248] that is

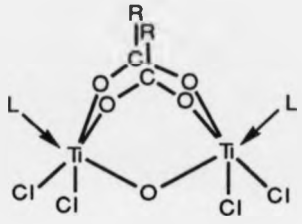
$$[TiCl_3(O_2CCMe_3)] + 2(MeCO)_2CH_2 \longrightarrow [TiCl_2\{(MeCO)_2CH\}_2] + HCl + Me_3CCO_2H$$

However, with dibenzoylmethane, $(PhCO)_2CH_2$, only the carboxylate group is displaced as free carboxylic acid and the trichlorotitanium(IV) product [$TiCl_3${$(PhCO)_2CH$}] is obtained.

Reactions with ligands such as pyridine (py), THF, NEt_3 and PPh_3 cause degradation of the complex and the formation of adducts such as $TiCl_4$.2py which can be isolated in low yield.[248] These observations are in contrast to those of Kapoor and co-workers who isolated compounds of the type [$TiCl_3(O_2CMe)$].2py and [$TiCl_3(O_2CR)$].py (R=Et, ^{n}Pr, ^{n}Bu or ^{n}Pentyl) under similar conditions.[174]

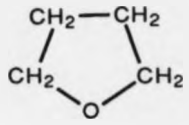
3.6. RESULTS AND DISCUSSION

In the previous chapter we have seen that species of the type $[Ti_2Cl_7(O_2CR)(RCO_2H)]$ (R=Et, CMe_3) and $[\{TiCl_2(O_2CR)(RCO_2H)\}_2O]$ (R=Me, Et, CMe_3) may be prepared by reacting differing ratios of $TiCl_4$ and the respective carboxylic acid at room temperature. The co-ordinating acid behaves similarly to other donor ligands such as THF or ethyl acetate in compounds of the type $[\{TiCl_2(O_2CR)L\}_2O]$ (R=Me, CMe_3, Ph ; L=THF, $MeCO_2Et$) **(3.10)** where the ligand takes up the sixth position around the octahedral titanium centre.[193]



R=Me, CMe_3, Ph
L=THF, $MeCO_2Et$

(3.10)



(3.11)

However, unlike these other donor ligands, the co-ordinating acid has the ability to hydrogen bond through the hydroxyl hydrogen, as is observed in the compounds of the formula $[\{TiCl_2(O_2CR)(RCO_2H)\}_2O]$ where the hydroxyl hydrogen is orientated towards an oxygen of the bridging carboxylate anion.

On this basis, it was considered of interest to investigate the possibility of exchanging the co-ordinating acid ligand with another donor molecule such as THF **(3.11)** which has the ability to co-ordinate to the metal centre through its etheral oxygen as in the dimeric halogen-bridged adduct $[\{TiCl_4.THF\}_2]$.[64]

In addition to this, the derivative $[\{Ti_2OCl_3(O_2CEt)_3(EtCO_2H)\}$ has not been structurally characterised, and therefore any information concerning the arrangement of the ligands around the metal atom in this compound would be useful. The addition of a small amount of THF to a solution of this latter compound could induce changes which may be indicative of one or possibly both of the following factors.

(i) that the compound contains co-ordinatively replaceable carboxylic acid ligands,

(ii) that the compound has co-ordinatively unsaturated titanium centres, therefore addition compounds could be prepared.

Replacement of the carboxylic acid ligand in the compounds of the type $[\{TiCl_2(O_2CR)(RCO_2H)\}_2O]$ should produce the corresponding free carboxylic acid in the reaction liquors as demonstrated by the equation below.

$$[\{TiCl_2(O_2CR)(RCO_2H)\}_2O] + 2THF \xrightarrow{\text{solvent}} [\{TiCl_2(O_2CR)THF\}_2O] + 2RCO_2H$$
$$(R=Me, Et, CMe_3)$$

The formation of free carboxylic acid may be corroborated by analysing the IR spectra of the reaction liquors for each exchange reaction undertaken.

The results of these experiments will now be discussed.

3.6.1. Preparation of compounds of the type $[\{TiCl_2(O_2CR)THF\}_2O]$ (R=Me, Et, CMe_3)

The compounds $[\{TiCl_2(O_2CR)(RCO_2H)\}_2O]$ (R=Me, Et, CMe_3) were prepared and isolated as previously discussed, then redissolved (R=Et, CMe_3) or suspended (R=Me) in toluene at room temperature. To the stirred solution the required stoichiometric amount of THF, given by the equation below, was added dropwise and the resultant reaction mixture was allowed to stir for 15 minutes.

$$[\{TiCl_2(O_2CR)(RCO_2H)\}_2O] + 2THF \xrightarrow{\text{solvent}} [\{TiCl_2(O_2CR)THF\}_2O] + 2RCO_2H$$
$$(R=Me, Et, CMe_3)$$

The final compounds were isolated by precipitation on the addition of light petroleum ether and elemental analysis indicated the composition $[\{TiCl_2(O_2CR)THF\}_2O]$. The title compounds were prepared in 80-90% yield and further characterised by their ^1H NMR and IR spectra.

IR Spectra of the species [{$TiCl_2(O_2CR)THF\}_2O$] (R=Me, Et, CMe_3)

IR spectra of the titled compounds were recorded in the region of 4000-200cm^{-1} and showed certain similarities with the corresponding carboxylic acid donor derivatives.

On comparing the IR spectra of these two types of compound it is apparent that the broad υ(OH) of the co-ordinated acid has disappeared as has the co-ordinated acid carbonyl signal at about 1650cm^{-1}. This region is now clear, as the bands arising from the THF ligand are observed at lower frequencies. Free THF exhibits $\upsilon(C\text{-}O\text{-}C)_{asym}$ at 1071 and $\upsilon(C\text{-}O\text{-}C)_{sym}$ at 909cm^{-1} but on co-ordination to the titanium metal centre these values move to lower wavenumbers; 1010 and 857 (R=Me), 1012 and 855 (R=Et), and 1009 and 858cm^{-1} (R=CMe_3) for the asymmetric and symmetric υ(C-O-C) stretching modes respectively.[249] The downward shift of these absorption bands in the IR spectra of the [{$TiCl_2(O_2CR)THF\}_2O$] species is, on average, 61 and 52 cm^{-1} for $\upsilon(C\text{-}O\text{-}C)_{asym}$ and $\upsilon(C\text{-}O\text{-}C)_{sym}$, which is comparable to the shift observed on co-ordination of the carboxylic acid ligand to the metal atom (*ca* 60cm^{-1}), in the analogous acid compounds. Thus the THF molecule co-ordinates to the titanium centre through the etheral oxygen.

The asymmetric and symmetric carboxylate stretching bands are very similarly positioned to those which occur in the IR spectra of the co-ordinated acid species (Table 2.6). The carboxylate absorption bands for the compounds [{$TiCl_2(O_2CR)THF\}_2O$] (R=Me, Et, CMe_3) are shown in Table 3.5 overpage, along with other relevant IR data.

Again, as with the species [{$TiCl_2(O_2CR)(RCO_2H)\}_2O$] we can see that the Δ values [$\upsilon(COO)_{asym}$-$\upsilon(COO)_{sym}$] of 100 (R=Me), 101 (R=Et) and 105cm^{-1} (R=CMe_3) indicate a symmetrical chelating or bridging mode. As it is believed that no rearrangement of the $[Ti_2O(O_2CR)_2]^{4+}$ framework has occurred, then the Δ values are in accord with the carboxylates being in a bridging co-ordination mode, thus supporting the proposed theory of Deacon and Phillips.[117]

Table 3.5 Major IR bands (cm^{-1}) of $[\{TiCl_2(O_2CR)THF\}_2O]$ (R=Me, Et, CMe_3) species.

R	$\upsilon(COO)_{asym}$	$\upsilon(COO)_{sym}$	Δ	υ(Ti-O-Ti)	$\upsilon(COC)_{asym}$*	$\upsilon(COC)_{sym}$*	υ(Ti-Cl) terminal
Me	1547	1447	100	723	1010	857	430, 421 380, 355
Et	1531	1430	101	725	1012	855	430, 420 400, 350
CMe_3	1525	1420	105	724	1009	858	453, 390 350

* Values for coordinated THF ligand

Free THF ligand has $\upsilon(COC)_{asym}$ at 1071, and $\upsilon(COC)_{sym}$ at 909cm^{-1}.

It should be noted at this point that the compounds $[\{TiCl_2(O_2CMe)THF\}_2O]$ and $[\{TiCl_2(O_2CCMe_3)THF\}_2O]$ have been previously prepared in this laboratory by the hydrolytic route, different to the one discussed here.[195] In the former route, the corresponding monocarboxylate $[TiCl_3(O_2CR)]$ (R=Me, CMe_3) was hydrolysed in a solution of THF, and both were characterised by elemental analysis, IR spectra and ^1H NMR spectra. The IR spectral data for these compounds has been discussed in Chapter 2 and some of the major absorption bands are displayed in Table 2.7.

The preparation of these compounds for this thesis has been accomplished *via* a different route by the non-hydrolytic formation of the species $[\{TiCl_2(O_2CR)(RCO_2H)\}_2O]$ and then subsequent displacement of the co-ordinating acid by the THF ligand. Both routes require a differing stoichiometry of reactant, that is, the $TiCl_4$ to carboxylic acid ratio for these latter compounds is required to be 1:2.5. The two possible routes are shown in the following schemes .

Hydrolytic route

$$TiCl_4 + RCO_2H \longrightarrow [TiCl_3(O_2CR)] + HCl$$

$$2[TiCl_3(O_2CR)] + H_2O + 2THF \longrightarrow [\{TiCl_2(O_2CR)THF\}_2O] + 2HCl$$

Non-hydrolytic route

$$2TiCl_4 + 5RCO_2H \longrightarrow [\{TiCl_2(O_2CR)(RCO_2H)\}_2O] + 3HCl + 2RCOCl$$

$$[\{TiCl_2(O_2CR)(RCO_2H)\}_2O] + 2THF \longrightarrow [\{TiCl_2(O_2CR)THF\}_2O] + 2RCO_2H$$

The yields of $[\{TiCl_2(O_2CMe)THF\}_2O]$ (R=Me, CMe_3) from each route differ considerably. It can be seen from Table 3.6 that the hydrolytic route affords a lower yield in the preparation of the THF adducts compared to the non-hydrolytic scheme, possibly due to the formation of other hydrolysis species which were soluble in the solution when $[\{TiCl_2(O_2CR)THF\}_2O]$ (R=Me, CMe_3) were isolated. It is therefore evident that the non-hydrolytic route presents a more controlled pathway in the formation of titanium oxo species of this type.

Table 3.6 Preparative yields of the compounds $[\{TiCl_2(O_2CR)THF\}_2O]$ (R=Me, Et, CMe_3)

Compound	Hydrolytic route	Non-hydrolytic route
$[\{TiCl_2(O_2CMe)THF\}_2O]$	55%	86%
$[\{TiCl_2(O_2CEt)THF\}_2O]$	a	79%
$[\{TiCl_2(O_2CCMe_3)THF\}_2O]$	30%	90%
[a] not prepared by this method		

As was previously discussed, compounds of the type $[\{TiCl_2(O_2CR)(RCO_2H)\}_2O]$ (R=Me, Et, CMe_3) exhibit a broad absorption band centred around 735cm^{-1} which can be assigned to a Ti-O-Ti stretching signal. Similarly, for compounds of the type $[\{TiCl_2(O_2CR)THF\}_2O]$ (R=Me, Et, CMe_3) a broad band is observed at 723 (R=Me), 725 (R=Et) and 724cm^{-1} (R=CMe_3) which implies that the μ_2-oxo framework is still intact. This would be expected, as it is only the terminal neutral carboxylic acid ligand which has been

removed and replaced with a molecule of THF, which leaves the structure essentially unchanged and of the same general geometry.

The absorption region between 1200-400cm^{-1} in the IR spectra of the compounds [{$TiCl_2(O_2CMe)(MeCO_2H)\}_2O$] (a) and [{$TiCl_2(O_2CMe)THF\}_2O$] (b) are shown for comparison below in Figure 3.1 overpage. In spectrum (a) we can see the broad υ(Ti-O-Ti) band associated with the $[Ti_2O(O_2CMe)_2]^{4+}$ unit. This is demonstrated also in spectrum (b) for the adduct of analogous structure, which in addition, displays the THF absorption bands of $\upsilon(C\text{-}O\text{-}C)_{asym}$ and $\upsilon(C\text{-}O\text{-}C)_{sym}$, indicating the presence of co-ordinated THF.

The Ti-Cl bonds in the compounds [{$TiCl_2(O_2CR)THF\}_2O$] should all be terminal if their structure is analogous to [{$TiCl_2(O_2CR)(RCO_2H)\}_2O$]. The Ti-Cl stretching bands are in close agreement with those values recorded previously for the co-ordinating acid species (Table 2.6) and are assigned at 430, 421, 380, 355 (R=Me), 430, 420, 400, 350 (R=Et) and 453, 390, 350cm^{-1} ($R=CMe_3$).

^{1}H NMR Spectra of [{$TiCl_2(O_2CR)THF\}_2O$] (R=Me, Et, CMe_3)

The ^{1}H NMR spectra of the title compounds and [{$TiCl_2(O_2CR)(RCO_2H)\}_2O$] (R=Me, Et, CMe_3) show many similarities. The respective THF and carboxylate signals were in the correct relative ratio for the title formulation. Again the methyl and methylene carboxylate signals exhibited multiplets at δ2.23-1.85 (R=Me), δ2.63-2.47 and 1.27-1.15 (R=Et) and δ1.34-1.25 ($R=CMe_3$). The co-ordinated THF methylene signals occur as broad singlets at δ4.8 and 2.23 (R=Me), δ4.9 and 2.22 (R=Et) and δ4.8 and 2.20 ($R=CMe_3$). No hydroxyl proton is observed in the spectra of these compounds thus indicating the complete replacement of the carboxylic acid ligands for the THF molecules.

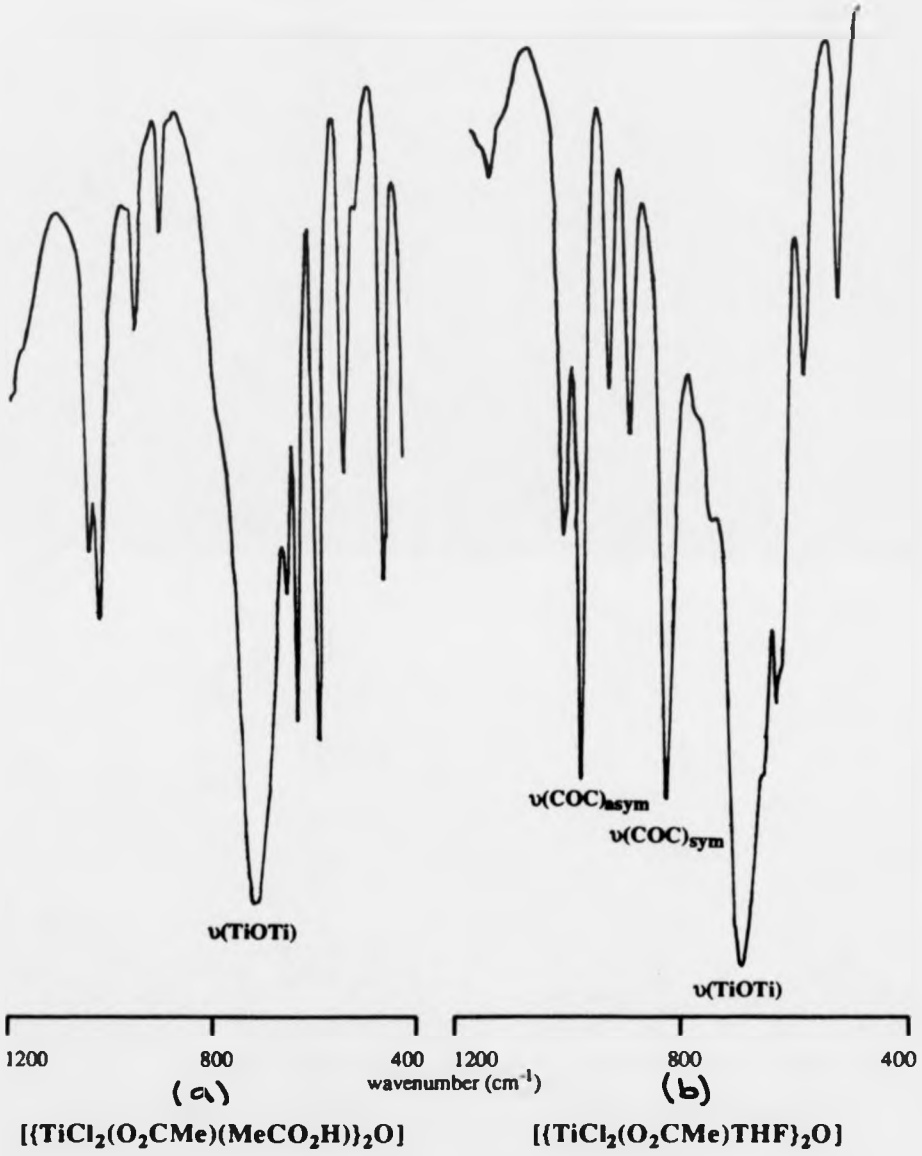


Figure 3.1 IR Spectra of the compounds $[\{TiCl_2(O_2CMe)(MeCO_2H)\}_2O]$ and $[\{TiCl_2(O_2CMe)THF\}_2O]$ in the region 1200-400cm^{-1}.

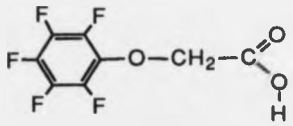
3.6.2. The Reaction of $[Ti_2OCl_3(O_2CEt)_3(EtCO_2H)]$ with THF

It is interesting to note in contrast to the reaction of $[\{TiCl_2(O_2CR)(RCO_2H)\}_2O]$ (R=Me, Et, CMe_3) with THF, that the title compound does not undergo any reaction with the donor molecule at room temperature and remains essentially unchanged when recovered from solution. This may indicate that the co-ordinating carboxylic acid is more strongly bonded to the titanium metal centre than in compounds of the type $[\{TiCl_2(O_2CR)(RCO_2H)\}_2O]$, and is less easily displaced by a THF molecule at room temperature. Displacement may possibly occur at higher temperatures.

3.6.3. Reaction of $TiCl_4$ with Pentafluorophenoxyacetic Acid in the Formation of $[\{TiCl_2(O_2CCH_2OC_6F_5)\}_2O]$

We have seen through the previous discussion that the species $[\{TiCl_2(O_2CR)(RCO_2H)\}_2O]$ (R=Me, Et, CMe_3) are able to exchange the co-ordinating carboxylic acid ligands for THF molecules to produce the compounds $[\{TiCl_2(O_2CR)THF\}_2O]$ which have an analogous structure.

It was of interest to extend this range of compounds to examine whether changes in the carboxylic acid structure had an effect on the stoichiometry of the final compound. Aromatic acids have been previously used in these laboratories in conjunction with $TiCl_4$ and have provided interesting and novel high temperature titanium species such as $[Ti_3O_2Cl_3(O_2CC_6H_4Me\text{-}p)_5]$[192] and the tetranuclear $[Ti_4O_2Cl_6(O_2CPh)_6]$[191] which will be discussed in greater detail in Chapter 4. Here for this thesis, the stronger fluoro-aromatic acids were used in the reaction with titanium tetrachloride. One of the acids chosen was pentafluorophenoxyacetic acid **(3.12)** since this has the added ability of acting as an ether due to it containing the C-O-C moiety which may co-ordinate to the metal centre instead of, or in addition to the carboxylate oxygens. It is a strong acid in comparison with the alkyl acids which have been previously used in the preparation of the $[\{TiCl(O_2CR)(RCO_2H)\}_2O]$ species.



$C_6F_5OCH_2CO_2H$

(3.12)

The reaction between pentafluorophenoxyacetic acid and $TiCl_4$ was carried out at room temperature with various reactant ratios being investigated. The product which was isolated after stirring the reaction mixture for 1 hour was independent of the reactant ratio and was formulated as $[\{TiCl_2(O_2CCH_2OC_6F_5)\}_2O]$. This next section will be assigned to discussing the preparation and spectral properties of this pentafluorophenoxyacetate compound.

Preparation of $[\{TiCl_2(O_2CCH_2OC_6F_5)\}_2O]$

Reaction of $TiCl_4$ with pentafluorophenoxyacetic acid in a 2:3 molar ratio, in benzene solvent at ambient temperature affords the compound $[\{TiCl_2(O_2CCH_2OC_6F_5)\}_2O]$ which is precipitated from the solution after 1-2 minutes as a fibrous yellow product in 65-70% yield. The reaction appears to proceed as follows:

$$2TiCl_4 + 3C_6F_5OCH_2CO_2H \longrightarrow [\{TiCl_2(O_2CCH_2OC_6F_5)\}_2O] + C_6F_5OCH_2COCl + 3HCl$$

The product $[\{TiCl_2(O_2CCH_2OC_6F_5)\}_2O]$ was identified by elemental analysis and further by IR and ^1H NMR spectroscopy which will be discussed in the following section.

IR Spectrum of $[\{TiCl_2(O_2CCH_2OC_6F_5)\}_2O]$

It is noticeable, by comparison with the IR spectra of the alkyl acid species $[\{TiCl_2(O_2CR)(RCO_2H)\}_2O]$ (R=Me, Et, CMe_3) that a broad co-ordinated acid hydroxyl absorption band is not present at 3200cm^{-1} in the IR spectrum of the title compound. Thus, it may be proposed, that the structure of the compound is not analogous to those reported in the previous Chapter.

The pentafluorophenoxyacetate derivative has three absorption bands in the carboxylate region of 1700-1400cm^{-1} which may be tentatively assigned as asymmetric and symmetric carboxylate stretching modes as shown in Table 3.7, which also displays other relevant IR data for [{$TiCl_2(O_2CCH_2OC_6F_5)$}$_2$O].

Table 3.7 Major absorption bands (cm^{-1}) in the IR spectrum of [{$TiCl_2(O_2CCH_2OC_6F_5)$}$_2$O]

$\upsilon(COO)_{asym}$	$\upsilon(COO)_{sym}$	Δ	υ(Ti-O-Ti)	$\upsilon(Ti\text{-}Cl)_{terminal}$
1626 1587	a 1450	- 137	735	448,421,385,345
[a] possibly assigned at 1523cm^{-1}				

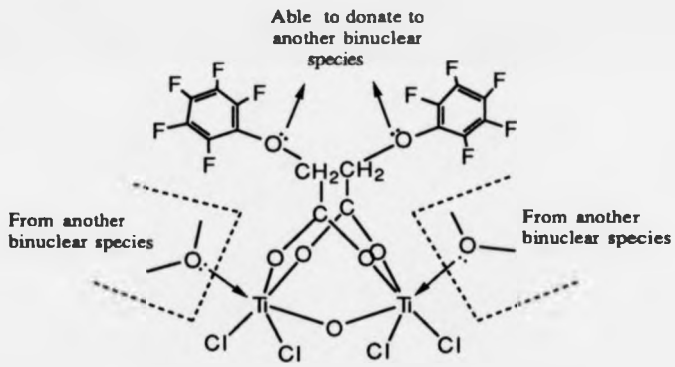
Due to the slight broadness of the absorption band situated at 1523cm^{-1} it is possible that a further carboxylate band is also present at, or near this frequency. If so, then Δ values of 103 (1626-1523) and 137cm^{-1} (1587-1450cm^{-1}) may be calculated. Both of these values of Δ are indicative of either chelating or bridging pentafluorophenoxyacetate groups, and due to the small number of chelating titanium carboxylate systems, the bridging co-ordination mode would be the most likely. On the basis of the proposed structure given below it is unclear, at present, why [{$TiCl_2(O_2CCH_2OC_6F_5)$}$_2$O] should exhibit two sets of carboxylate stretching modes especially in view of the ^{1}H NMR data for this compound.

It can be seen from the IR spectrum that the strong υ(C-O-C) stretching band of the alkyl ether moiety in the free carboxylic acid has reduced greatly in intensity and moved to lower wavenumbers. This shift from 1067 to 1038cm^{-1} giving a value 29cm^{-1} is indicative of co-ordination of the etheral oxygen to the titanium metal centre. This has previously been seen in compounds of the type [{$TiCl_2(O_2CR)THF$}$_2$O] (R=Me, Et, CMe_3) where the co-ordinated THF asymmetric and symmetric υ(C-O-C) absorption bands have moved to lower wavenumbers by *ca.* 60cm^{-1} from those found in the free ligand. The shift of 29cm^{-1}

observed here is clearly smaller than that of the alkyl derivatives, possibly due to a lesser Ti-O interaction.

The co-ordination of the etheral oxygen of the pentafluorophenoxyacetate ligand suggests that the acid is acting as a terdentate donor, with the two carboxylate oxygens bridging two titanium atoms and the oxygen of the alkyl chain co-ordinating to the sixth site of a neighbouring titanium to give a structure similar to that outlined below **(3.13)**.

In this way each molecule associates with two others through the etheral oxygen atoms of the bridging carboxylate groups to co-ordinate to the titanium atom at the vacant sixth position. This could possibly explain why, with a reaction mixture containing excess carboxylic acid the compound $[\{TiCl_2(O_2CCH_2OC_6F_5)(C_6F_5OCH_2CO_2H\}_2O]$ is not formed and $[\{TiCl_2(O_2CCH_2OC_6F_5)\}_2O]$ remains unchanged.



(3.13)

As was seen with experiments concerning $[\{TiCl_2(O_2CR)(RCO_2H\}_2O]$ (R=Me, Et, CMe_3), the addition of THF to their solutions produced analogous adducts with the THF ligand displacing the carboxylic acid and co-ordinating to the metal centre. It seems likely, therefore, that a similar situation occurs here, and the etheral oxygen of the acid co-ordinates in preference to the carboxylic acid, thus making the titanium atom co-ordinatively saturated.

Also supporting the postulated structural unit **(3.13)** displayed above, is the presence of a medium intensity band situated at $735cm^{-1}$ which may be assigned to $\upsilon(Ti\text{-}O\text{-}Ti)_{asym}$ of the μ_2-oxo bridge. It is of lower intensity and less broad than the

analogous bands of the species [{$TiCl_2(O_2CR)(RCO_2H\}_2O$] (R=Me, Et, CMe_3), which may possibly be a consequence of the highly associated structure of the pentafluorophenoxyacetate derivative.

Terminal Ti-Cl stretching vibrations may be assigned to bands at 448, 421, 385 and 345cm^{-1}.

^1H NMR spectrum of [{$TiCl_2(O_2CCH_2OC_6F_5)\}_2O$]

The ^1H NMR spectrum in d^8 toluene of the title compound does not appear to have a broad signal attributed to the acid hydroxyl in the range δ11.5-7.0, which would tend to indicate the absence of co-ordinated carboxylic acid ligands. Two doublets are apparent, centred at δ5.23(1H) and 4.98(1H) which suggests that the two methylene protons of the acid are in differing environments and therefore inequivalent. The spin-spin coupling constant, J, for each doublet is 15Hz. This inequivalence is not seen in the free carboxylic acid ^1H NMR spectrum which displays a signal at δ4.05.

Thus, the data would tend to imply that the methylene protons in [{$TiCl_2(O_2CCH_2OC_6F_5)\}_2O$] are in a fixed position and are unable to rotate around the carbon axis. The inequivalence could possibly be the result of the ethereal oxygen of a bridging carboxylate ligand co-ordinating to an adjacent titanium atom and therefore making the carboxylate structure more rigid and unable to rotate. The ^1H NMR of [{$TiCl_2(O_2CCH_2OC_6F_5)\}_2O$] is shown in Figure 3.2.

Further evidence for oxygen donation to an adjacent metal atom comes from the downfield shift of methylene protons from δ4.05 in the free carboxylic acid to δ5.23 and 4.98 in the compound. This move to lower field would be a consequence of electron withdrawal from the methylene protons.

A large amount of solvent is present in the compound as is apparent from methylene and methyl proton signals at δ1.22 and 0.89 respectively. From the integrals, this would approximate to a ratio of 1: 0.5 for [{$TiCl_2(O_2CCH_2OC_6F_5)\}_2O$] : C_6H_{14}. The

hexane (b.p. 60-80°C fraction) was used to wash the final compound, and evidently was unable to be removed on pumping for 4 hours.

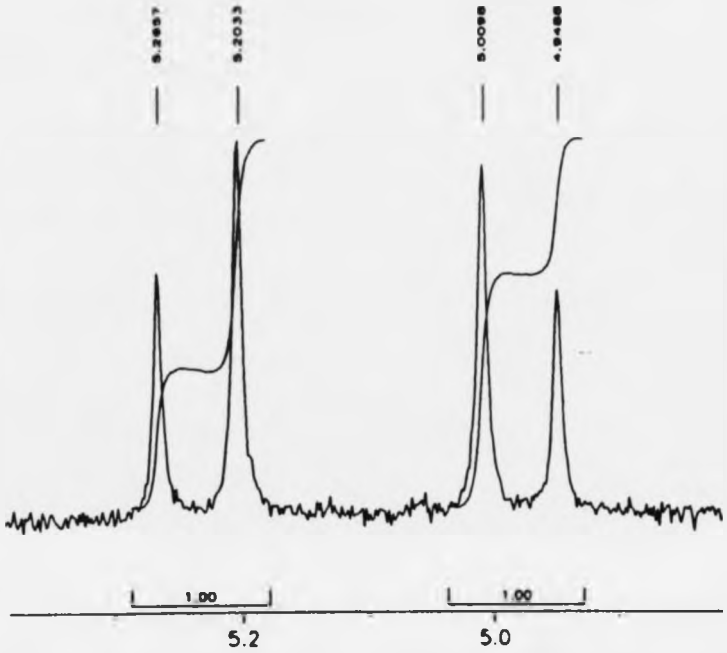


Figure 3.2 The ^1H NMR spectrum of the compound $[\{TiCl_2(O_2CCH_2OC_6F_5)\}_2O]$ indicating the inequivalence of the methylene protons

In summary, the compound $[\{TiCl_2(O_2CCH_2OC_6F_5)\}_2O]$ is proposed as a binuclear species with the titanium atoms linked by two bridging carboxylate groups and a (μ_2-O) bridge. The chlorine ligands are all terminal, as indicated by the absence of Ti-Cl-Ti bridging stretching bands in the IR spectrum. The proposed structure is similar to that of the species $[\{TiCl_2(O_2CR)(RCO_2H)\}_2O]$ (R=Me, Et, CMe_3) which also contains the $[Ti_2O(O_2CR)_2]^{4+}$ core, but the sixth position of each titanium atom in the pentafluorophenoxyacetate derivative is taken up by the ethereal oxygen atom of an adjacent molecule. This association could account for the poor solubility of $[\{TiCl_2(O_2CCH_2OC_6F_5)\}_2O]$ in aromatic and chlorinated solvents, and the good solubility in polar donor solvents such as THF and acetonitrile which could displace the acid ethereal

oxygen from the sixth co-ordination position around the titanium atoms, and produce new species such as $[\{TiCl_2(O_2CCH_2OC_6F_5)THF\}_2O]$ and $[\{TiCl_2(O_2CCH_2OC_6F_5)MeCN\}_2O]$.

3.6.4. Preparation of $[\{TiCl_2(O_2CCH_2OC_6F_5)THF\}_2O]$

Following on from these observations, it has been possible to isolate the compound $[\{TiCl_2(O_2CCH_2OC_6F_5)THF\}_2O]$ in high yield from the addition of THF to a solution of $[\{TiCl_2(O_2CCH_2OC_6F_5)\}_2O]$, thus adding more evidence for the postulated structure.

The title compound may be prepared in a two stage process, namely isolation of $[\{TiCl_2(O_2CCH_2OC_6F_5)\}_2O]$ followed by the treatment of a suspension of this material in benzene with the addition of THF according to the equation below.

$$[\{TiCl_2(O_2CCH_2OC_6F_5)\}_2O] + 2THF \xrightarrow{\text{benzene}} [\{TiCl_2(O_2CCH_2OC_6F_5)THF\}_2O]$$

The same product may also be isolated more conveniently from a 'one pot' process as outlined below.

Thus the addition of $TiCl_4$ (2 mol) to a solution of pentafluorophenoxyacetic acid (3 mol) in benzene, and the subsequent addition of THF (2 mol) to this reaction mixture at room temperature, produces a red solution. After stirring for 30 minutes the yellow THF product is precipitated from solution in *ca.* 85-90% yield by the addition of a large amount of petroleum ether.

$$2TiCl_4 + 3C_6F_5OCH_2CO_2H + 2THF \longrightarrow$$
$$[\{TiCl_2(O_2CCH_2OC_6F_5)THF\}_2O] + C_6F_5OCH_2COCl + 3HCl$$

The product may be recrystallised by slow diffusion from a dichloromethane solution layered with petroleum ether to give yellow block-like crystals.

$[\{TiCl_2(O_2CCH_2OC_6F_5)THF\}_2O]$ was fully characterised by X-ray diffraction, and in addition by elemental analysis, IR and ^1H NMR spectroscopy. The spectral studies and structural characterisation are presented below.

IR Spectral data for $[\{TiCl_2(O_2CCH_2OC_6F_5)THF\}_2O]$

The IR spectrum of $[\{TiCl_2(O_2CCH_2OC_6F_5)THF\}_2O]$ shows carboxylate absorption bands at 1595 [$\upsilon(COO)_{asym}$] and 1450cm^{-1} [$\upsilon(COO)_{sym}$] which gives a Δ value of 145cm^{-1}. This, as has been discussed previously, is consistent with the presence of bridging carboxylate groups. Crystal structure analysis shows that the pentafluorophenoxyacetate ligands are symmetrically bridging, therefore again indicating that the measurement of Δ values has some reliability in the detection of the carboxylate bonding mode.

Absorption bands in the region 1200-900cm^{-1} contain υ(C-O-C) vibrations, and are virtually unchanged from those found in the free acid spectrum. This region is also unlike that found in the spectrum of $[\{TiCl_2(O_2CCH_2OC_6F_5)\}_2O]_n$ which contains ethereal oxygen co-ordination to the metal, thus indicating distinct differences between the two compounds.

The THF absorption bands can be identified at 990 for $\upsilon(C\text{-}O\text{-}C)_{asym}$ and at 837cm^{-1} for $\upsilon(C\text{-}O\text{-}C)_{sym}$. These values are in accord with those found for the related systems of the acetate, propanoate and trimethylacetate as discussed earlier in this Chapter. A comparison of the major absorption bands of the species $[\{TiCl_2(O_2CR)THF\}_2O]$ (R=Me, Et, CMe_3, $CH_2OC_6F_5$) is shown in Table 3.8.

Table 3.8 A comparison of the major bands in the IR spectra (cm^{-1}) of the species $[\{TiCl_2(O_2CR)THF\}_2O]$ (R=Me, Et, CMe_3, $CH_2OC_6F_5$).

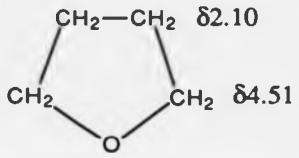
R	$\upsilon(COO)_{asym}$	$\upsilon(COO)_{sym}$	Δ	υ(Ti-O-Ti)	$\upsilon(COC)_{asym}$	$\upsilon(COC)_{sym}$	υ(Ti-Cl)
Me	1547	1447	100	723	1010	857	450, 421 380, 355
Et	1531	1430	101	725	1012	851	430, 420 400, 350
CMe_3	1525	1420	105	724	1009	858	453, 390 350
$CH_2OC_6F_5$	1595	1450	145	748	990	837	430, 415 380, 330

υ(Ti-O-Ti) can be detected as a medium intensity band at 748cm^{-1}, which is similar to that found for the compound [{$TiCl_2(O_2CCH_2C_6F_5)$}$_2$O] situated at 735cm^{-1} but of weaker intensity.

Ti-Cl terminal stretching absorption bands occur at 430, 415, 380 and 330cm^{-1}.

^{1}H NMR Spectrum of [{$TiCl_2(O_2CCH_2OC_6F_5)THF$}$_2$O]

The ^{1}H NMR spectrum ($CDCl_3$) of the title compound shows a singlet situated at δ4.86 which is due to equivalent methylene protons. The broad multiplets (1:1 ratio) centred at δ4.51 and 2.10 are assigned to the two sets of co-ordinated THF protons (**3.15**).



(3.15)

The ratio of methylene protons to THF protons is consistent with a 1:4 ratio as would be expected for the compound [{$TiCl_2(O_2CCH_2OC_6F_5)(OC_4H_8)$}$_2$O].

3.6.5. The X-Ray Crystal Structure of [{$TiCl_2(O_2CCH_2OC_6F_5)THF$}$_2$O]

Crystals suitable for X-ray diffraction were obtained from a dichloromethane / petroleum ether solution as yellow blocks.

The X-ray crystallographic study revealed the presence of the now familiar $[Ti_2(\mu_2\text{-}O)(\mu_2\text{-}O_2CR)_2]^{4+}$ core as has been discussed for the compounds [{$TiCl_2(O_2CR)(RCO_2H)$}$_2$O] (R=Et, CMe_3) in Chapter 2. The structure of [{$TiCl_2(O_2CCH_2OC_6F_5)THF$}$_2$O] is analogous to that of the carboxylic acid adduct derivatives and will therefore only be briefly discussed.

The structure of [{$TiCl_2(O_2CCH_2OC_6F_5)THF$}$_2$O] is shown in Figure 3.3, and bond lengths and bond angles are displayed in Tables 3.9 and 3.10 respectively.

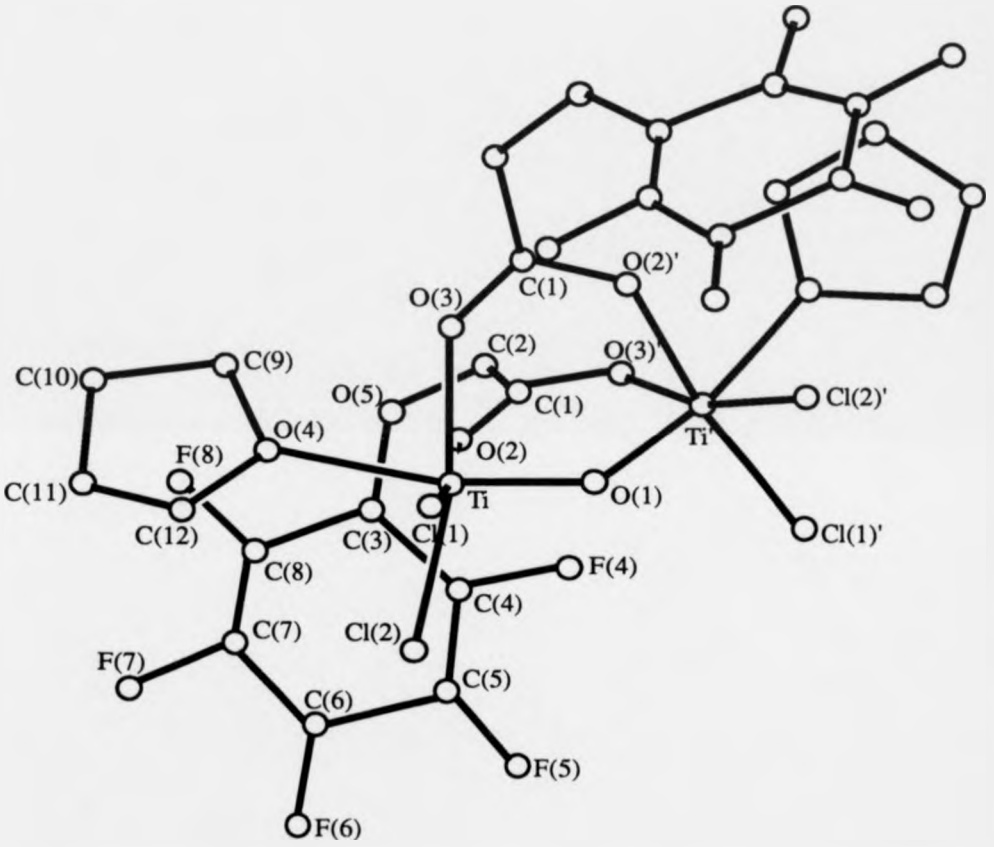


Figure 3.3 The X-ray crystal structure of $[\{TiCl_2(O_2CCH_2OC_6F_5)THF\}_2O]$.

Table 3.9 Bond lengths for $[\{TiCl_2(O_2CCH_2OC_6F_5)THF\}_2O]$ (Å)

Ti-Cl(1)	2.254(2)	Ti-Cl(2)	2.253(2)
Ti-O(1)	1.783(2)	Ti-O(2)	2.034(4)
Ti-O(4)	2.101(4)	O(2)-C(1)	1.248(7)
O(3)-C(1)	1.256(8)	O(4)-C(9)	1.441(9)
O(4)-C(12)	1.437(9)	O(5)-C(2)	1.415(8)
O(5)-C(3)	1.352(8)	C(1)-C(2)	1.498(9)
C(3)-C(4)	1.370(10)	C(3)-C(8)	1.381(11)
C(4)-C(5)	1.370(12)	C(4)-F(4)	1.340(9)
C(5)-C(6)	1.357(13)	C(5)-F(5)	1.329(11)
C(6)-C(7)	1.334(14)	C(6)-F(6)	1.347(12)
C(7)-C(8)	1.400(13)	C(7)-F(7)	1.341(11)
C(8)-F(8)	1.317(10)	C(9)-C(10)	1.474(12)
C(10)-C(11)	1.478(14)	C(11)-C(12)	1.457(13)

Table 3.10 Bond angles for [{$TiCl_2(O_2CCH_2OC_6F_5)THF$}$_2O$] (°)

Cl(2)-Ti-Cl(1)	98.2(1)	O(1)-Ti-Cl(1)	98.1(1)
O(1)-Ti-Cl(2)	98.0(1)	O(2)-Ti-Cl(1)	169.3(1)
O(2)-Ti-Cl(2)	88.5(1)	O(2)-Ti-O(1)	89.2(2)
O(4)-Ti-Cl(1)	89.9(1)	O(4)-Ti-Cl(2)	89.5(1)
O(4)-Ti-O(1)	168.1(2)	O(4)-Ti-O(2)	81.7(2)
Ti-O(1)-Ti	138.8(3)	C(1)-O(2)-Ti	132.5(4)
C(9)-O(4)-Ti	126.3(4)	C(12)-O(4)-Ti	124.7(4)
C(12)-O(4)-C(9)	109.0(6)	C(3)-O(5)-C(2)	119.9(5)
O(3)-C(1)-O(2)	125.9(6)	C(2)-C(1)-O(2)	117.3(6)
C(2)-C(1)-O(3)	116.8(5)	C(1)-C(2)-O(5)	114.4(6)
C(4)-C(3)-O(5)	127.9(6)	C(8)-C(3)-O(5)	113.8(6)
C(8)-C(3)-C(4)	118.2(7)	C(5)-C(4)-C(3)	121.6(7)
F(4)-C(4)-C(3)	120.3(7)	F(4)-C(4)-C(5)	118.1(7)
C(6)-C(5)-C(4)	119.4(9)	F(5)-C(5)-C(4)	119.4(8)
F(5)-C(5)-C(6)	121.2(9)	C(7)-C(6)-C(5)	120.9(9)
F(6)-C(6)-C(5)	119.1(9)	F(6)-C(6)-C(7)	120.0(9)
C(8)-C(7)-C(6)	120.5(9)	F(7)-C(7)-C(6)	122.4(9)
F(7)-C(7)-C(8)	117.0(8)	C(7)-C(8)-C(3)	119.3(8)
F(8)-C(8)-C(3)	120.4(7)	F(8)-C(8)-C(7)	120.3(8)
C(10)-C(9)-O(4)	107.1(7)	C(11)-C(10)-C(9)	105.5(8)
C(12)-C(11)-C(10)	106.3(8)	C(11)-C(12)-O(4)	105.5(7)

Reference to Figure 3.3 reveals that the compound is binuclear with the two titanium atoms in near octahedral co-ordination. The metal atoms are joined by two symmetrical pentafluorophenoxyacetate ligands and a μ_2-oxo bridge. The Ti-O-Ti angle is bent at 138.8° which is similar to that found in $[\{TiCl_2(O_2CR)(RCO_2H)\}_2O]$ (R=Et, 137.3°; R=CMe_3, 138.3°) and $[\{TiCl_2(O_2CPh)MeCO_2Et\}_2O]$ where the μ_2-oxo bridge subtends an angle of 137.2°.[193] Now that a number of structures have been determined, the stability and similar geometries of the $[M(\mu_2\text{-}O)(\mu_2\text{-}O_2CR)_2M]^{n+}$ unit is becoming more apparent. The remarkably small variation in the Ti-O-Ti angles over several different types of derivatives testifies further to this particular point. The carboxylate O-C-O angle has opened up to 125.9° from the ideal 120° around an sp^2 hybridised carbon atom, and the angle Ti-O(2)-C(1) also deviates from 120° to 132.5°.

The three non-bridging positions on each metal are occupied by two chlorine atoms and a THF molecule which is *trans* to the μ-oxo group.

The average Ti-O distances are graduated as Ti-μ_2-O (1.78Å) < Ti-μ-$O_{acid\ anion}$ (2.034Å) < Ti-O_{THF} (2.10Å), and the Ti-Cl distances (2.25Å) are within the expected values.

The orientation of the pentafluorophenoxyacetate ligand molecules is unremarkable, and both are situated so as to minimise intra- and inter- interactions, as shown by an examination of the crystal packing in the unit cell.

The angles around the titanium atoms are similar to those of the co-ordinated acid species $[\{TiCl_2(O_2CR)(RCO_2H)\}_2O]$ (R=Et, CMe_3) and for a more detailed discussion concerning this structural type, reference should be made of structural details in Chapter 2.

3.6.6. Study of the Reactions of $[\{TiCl_2(O_2CCMe_3)THF\}_2O]$ and the Products Obtained; Preparation of $[\{TiOCl(O_2CCMe_3)THF\}_4]$

During one experiment concerning the preparation of $[\{TiCl_2(O_2CCMe_3)THF\}_2O]$ from the analogous co-ordinated species, an unexpected and serendipitous hydrolysis reaction occurred. The water was eventually traced to the THF used in the reaction, and to the fact that the drying agent used was not completely effective due to an extended period of use. Thus on addition of the contaminated THF to $[\{TiCl_2(O_2CCMe_3)(Me_3CCO_2H)\}_2O]$ in toluene, a crystalline product was formed which precipitated from the solution when layered with light petroleum. The colourless crystals were formed in low yield (15%), indicating the small amount of water which was present in the THF. A crystal structure determination showed that the solid was a hydrolysis product, *viz.* $[\{TiOCl(O_2CCMe_3)THF\}_4]$, which contained a subsequently novel tetrameric structure, and is formed by the equation below.

$$2[\{TiCl_2(O_2CCMe_3)(Me_3CCO_2H)\}_2O] + 2H_2O + 4THF \longrightarrow [\{TiOCl(O_2CCMe_3)THF\}_4] + 4HCl + 4Me_3CCO_2H$$

$[\{TiOCl(O_2CCMe_3)THF\}_4]$ was able to be prepared in high yield by controlled hydrolysis experiments as will be outlined below. In addition to the structural determination, the compound was further characterised by elemental analysis along with IR and ^1H NMR spectroscopy.

When $[\{TiCl_2(O_2CCMe_3)(Me_3CCO_2H)\}_2O]$ (1 mol) is dissolved in toluene at room temperature, and a mixture of THF (2 mol) with water (1 mol) is added with stirring, the solution immediately turns from orange to very pale yellow. After stirring for a further 15 minutes the title product is precipitated from solution as a white powder by the addition of petroleum ether, in 80% yield.

In an analogous reaction, but without the addition of water to the THF, the species $[\{TiCl_2(O_2CCMe_3)THF\}_2O]$ was formed as expected. It is relevant to point out that the addition of water to $[\{TiCl_2(O_2CCMe_3)THF\}_2O]$ should also produce the species $[\{TiOCl(O_2CCMe_3)THF\}_4]$. However, experiments concerning the controlled hydrolysis

of this compound only resulted in oils being produced, which appeared to be a mixture of compounds.

Thus, the various reactions occurring may be summarised by the equations below.

Non-hydrolytic reaction

$$[\{TiCl_2(O_2CCMe_3)(Me_3CCO_2H)\}_2O] + 2THF \longrightarrow [\{TiCl_2(O_2CCMe_3)THF\}_2O] + 2Me_3CCO_2H$$

Hydrolytic reaction

$$2[\{TiCl_2(O_2CCMe_3)(Me_3CCO_2H)\}_2O] + 2H_2O + 4THF \longrightarrow [\{TiOCl(O_2CCMe_3)THF\}_4] + 4HCl + 4Me_3CCO_2H$$

A possible reaction pathway for the formation of the tetranuclear compound $[\{TiOCl(O_2CCMe_3)THF\}_4]$ is shown in Figure 3.4. It is suggested that following the hydrolysis of 2 units of $[\{TiCl_2(O_2CCMe_3)(Me_3CCO_2H)\}_2O]$ in the presence of THF ligands, the $[Ti_2(\mu_2\text{-}O)(\mu_2\text{-}O_2CCMe_3)_2]^{4+}$ core remains, and two further oxo bridges link the two units, with the concomitant evolution of HCl.

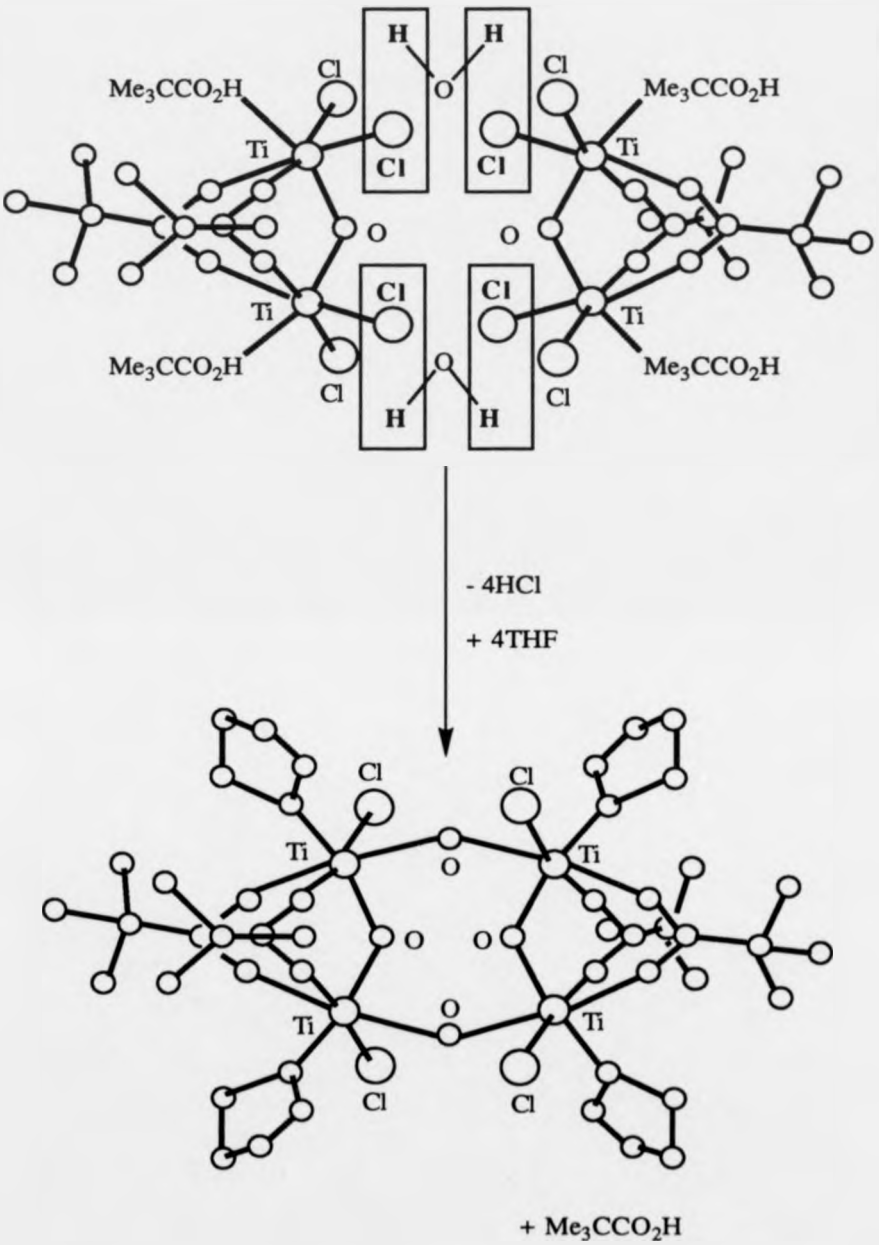


Figure 3.4 Representation of the hydrolytic reaction in the formation of $[\{TiOCl(O_2CCMe_3)THF\}_4]$.

IR Spectrum of [{TiOCl(O_2CCMe_3)THF}$_4$]

The IR spectrum of the title compound shows carboxylate absorption bands at 1575 [$\upsilon(COO)_{asym}$] and 1430cm^{-1} [$\upsilon(COO)_{sym}$], giving a Δ value of 145cm^{-1}. This is consistent with the values of Δ obtained for bridging carboxylate ligands in a $[Ti_2(\mu_2\text{-}O)(\mu_2\text{-}O_2CR)_2]^{4+}$ system that have been discussed in previous sections of this thesis.

Absorption bands at 1026 and 881cm^{-1} may be assigned to $\upsilon(C\text{-}O\text{-}C)_{asym}$ and $\upsilon(C\text{-}O\text{-}C)_{sym}$ of the co-ordinated THF ligands which have moved down 45 and 28cm^{-1} from the corresponding asymmetric and symmetric stretching band of the free ligand.

The broad strong band centred at 791cm^{-1} has shoulder bands on either side, and may be attributed to the Ti-O-Ti stretching vibrations of both the carboxylate supported and unsupported μ_2-oxo bridges.

An absorption band of medium intensity situated at 375cm^{-1} is designated as a terminal υ(Ti-Cl).

^{1}H NMR Spectrum of [{TiOCl(O_2CCMe_3)THF}$_4$]

The ^{1}H NMR spectrum shows broad singlets (relative intensities 1:1) at δ3.96 and 1.90 which can be attributed to the protons of the THF ligands, and a multiplet over the range δ1.38-1.11 which is assigned to the methyl protons of the bridging carboxylate ligand. The integrals of the signals are consistent with the title compound with δ3.96 (relative intensity 2), 1.90 (2) and 1.38-1.11 (9).

3.6.7 The X-Ray Crystal Structure of [{TiOCl(O_2CCMe_3)THF}$_4$]

Crystals suitable for X-ray diffraction studies were obtained from a solution of the title compound in toluene layered with petroleum ether by slow diffusion.

The structure of [{TiOCl(O_2CCMe_3)THF}$_4$] is shown in Figures 3.5 and 3.6, and the selected bond lengths and angles are displayed in Tables 3.11 and 3.12 respectively.

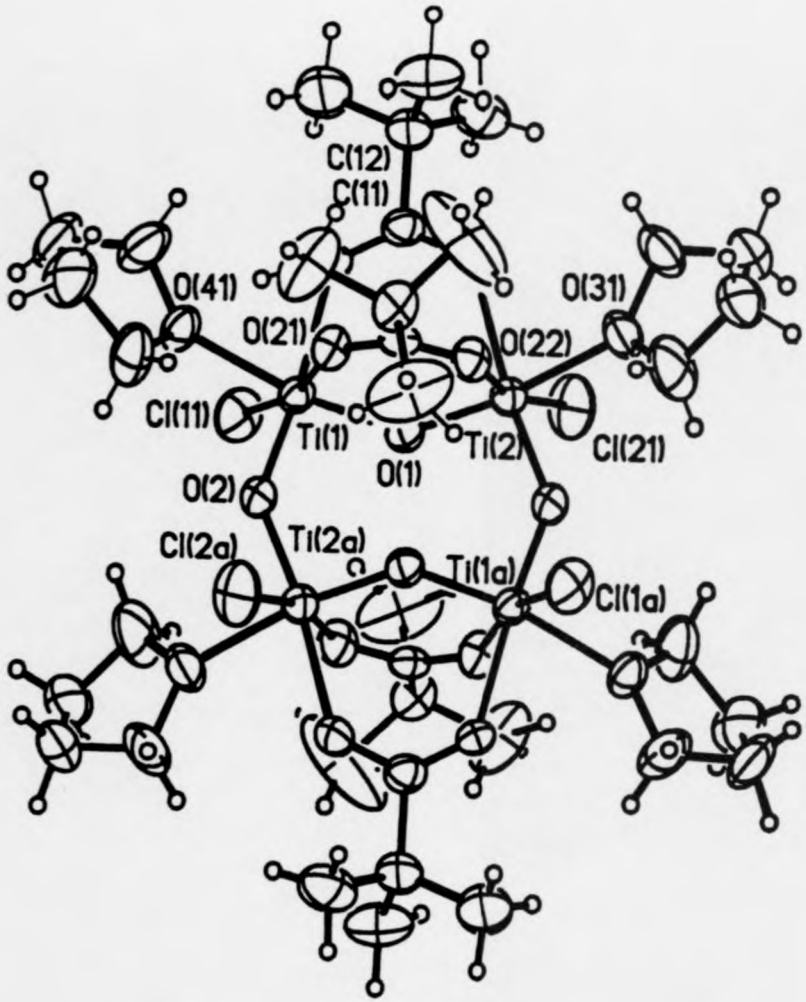


Figure 3.5 The X-ray crystal structure of $[\{TiOCl(O_2CCMe_3)THF\}_4]$

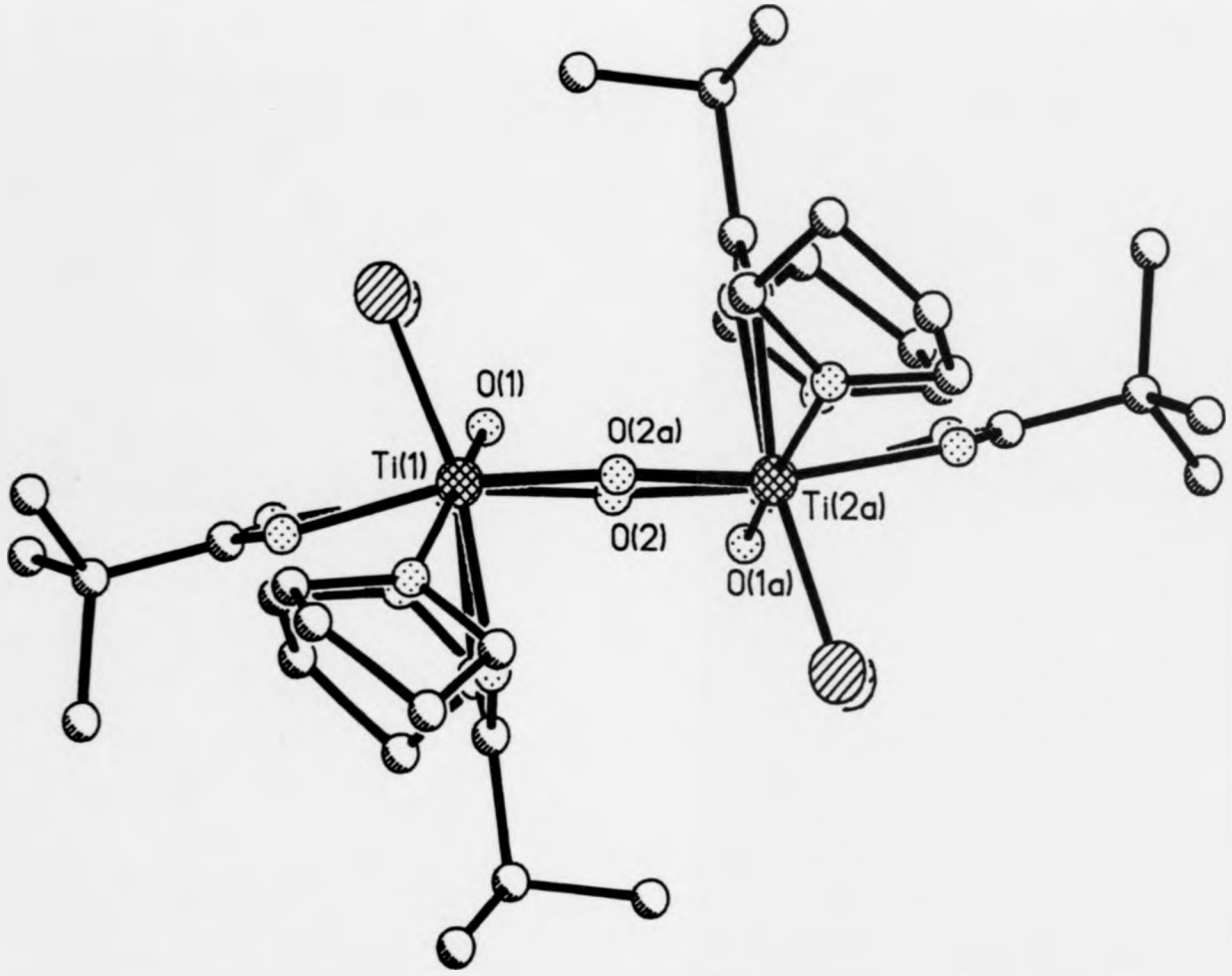


Figure 3.6 The view of $[\{TiOCl(O_2CCMe_3)THF\}_4]$ through the approximate plane of titanium atoms.

Table 3.11 Selected bond lengths of [{TiOCl(O_2CCMe_3)THF}$_4$] (Å)

Ti(1)-Ti(2)	3.358(3)	Ti(1)-Cl(11)	2.317(3)
Ti(1)-O(1)	1.827(4)	Ti(1)-O(2)	1.810(4)
Ti(1)-O(11)	2.111(4)	Ti(1)-O(21)	2.054(4)
Ti(1)-O(41)	2.152(4)	Ti(2)-Cl(21)	2.320(3)
Ti(2)-O(1)	1.799(4)	Ti(2)-O(12)	2.074(4)
Ti(2)-O(22)	2.045(5)	Ti(2)-O(31)	2.165(4)
Ti(2)-O(2a)	1.850(4)	O(2)-Ti(2a)	1.850(4)
O(11)-C(11)	1.258(7)	O(12)-C(11)	1.281(7)
O(21)-C(21)	1.262(7)	O(22)-C(21)	1.266(7)
O(31)-C(31)	1.462(7)	O(31)-C(34)	1.453(9)
O(41)-C(41)	1.468(8)	O(41)-C(44)	1.443(8)

Table 3.12 Selected bond angles of [{$TiOCl(O_2CCMe_3)THF$}$_4$] (°).

Cl(11)-Ti(1)-O(1)	98.8(1)	O(1)-Ti(1)-O(2)	98.6(2)
Cl(11)-Ti(1)-O(2)	99.1(1)	Cl(11)-Ti(1)-O(11)	89.1(1)
O(1)-Ti(1)-O(11)	88.0(2)	O(2)-Ti(1)-O(11)	168.6(2)
O(1)-Ti(1)-O(21)	92.0(2)	Cl(11)-Ti(1)-O(21)	165.5(1)
O(11)-Ti(1)-O(21)	81.5(2)	O(2)-Ti(1)-O(21)	88.9(2)
Cl(11)-Ti(1)-O(41)	87.7(1)	O(1)-Ti(1)-O(41)	169.1(2)
O(2)-Ti(1)-O(41)	89.0(2)	O(11)-Ti(1)-O(41)	83.2(2)
O(21)-Ti(1)-O(41)	80.3(2)	Cl(21)-Ti(2)-O(1)	98.3(1)
O(1)-Ti(2)-O(12)	89.7(2)	Cl(21)-Ti(2)-O(12)	88.9(1)
Cl(21)-Ti(2)-O(22)	165.1(1)	O(1)-Ti(2)-O(22)	93.1(2)
O(12)-Ti(2)-O(22)	81.7(2)	O(1)-Ti(2)-O(31)	170.2(2)
Cl(21)-Ti(2)-O(31)	87.5(1)	O(22)-Ti(2)-O(31)	79.9(2)
O(12)-Ti(2)-O(31)	82.5(2)	Cl(21)-Ti(2)-O(2a)	99.0(1)
O(1)-Ti(2)-O(2a)	99.9(2)	O(12)-Ti(2)-O(2a)	166.5(2)
O(22)-Ti(2)-O(2a)	88.3(2)	O(31)-Ti(2)-O(2a)	86.9(2)
Ti(1)-O(1)-Ti(2)	135.6(2)	Ti(1)-O(2)-Ti(2a)	139.7(4)
Ti(1)-O(11)-C(11)	132.0(4)	Ti(2)-O(12)-C(11)	133.2(4)
Ti(1)-O(21)-C(21)	135.2(4)	Ti(2)-O(22)-C(21)	132.7(4)
Ti(2)-O(31)-C(31)	128.1(4)	Ti(2)-O(31)-C(34)	123.2(4)
C(31)-O(31)-C(34)	108.7(5)	Ti(1)-O(41)-C(41)	122.4(3)
Ti(1)-O(41)-C(44)	127.8(4)	C(41)-O(41)-C(44)	109.5(5)
O(11)-C(11)-O(12)	125.0(5)	O(11)-C(11)-C(12)	120.4(5)
O(12)-C(11)-C(12)	114.6(5)	O(21)-C(21)-O(22)	123.8(6)
O(21)-C(21)-C(22)	117.6(5)	O(22)-C(21)-C(22)	118.7(5)
O(31)-C(31)-C(32)	105.3(5)	O(31)-C(34)-C(33)	106.6(6)
O(41)-C(41)-C(42)	104.7(5)	O(41)-C(44)-C(43)	105.0(6)

As can be seen by reference to Figures 3.5 and 3.6, the molecule is a tetranuclear species which contains a central Ti_4O_4 octameric ring of alternate titanium and oxygen atoms. The four titanium atoms are in a distorted octahedral environment and are coplanar with the two oxygen atoms O(2) and O(2a), whilst the other two oxygen atoms O(1) and O(1a) lie ~0.5Å above and below this plane. Pairs of titanium atoms are further linked by two trimethylacetate bridges to give the μ-oxo-bis-μ-carboxylate dinuclear fragment $[Ti_2(\mu_2\text{-}O)(\mu_2\text{-}O_2CR)_2]^{4+}$ which has been previously reported in this thesis for the compounds $[\{TiCl_2(O_2CEt)(EtCO_2H)\}_2O]$ *1*, $[\{TiCl_2(O_2CCMe_3)(Me_3CCO_2H)\}_2O]$ *2* and $[\{TiCl_2(O_2CCH_2OC_6F_5)THF\}_2O]$ *3*. The remaining two co-ordination positions on each titanium atom are occupied by a terminal chlorine atom and a co-ordinated THF ligand. The molecule is structurally very similar to the recently published tetranuclear tantalum(V) oxo cluster $[\{TaOCl_2(O_2C_6H_4Me\text{-}p)\}_4]$ which contains a chlorine atom in place of the THF ligands to maintain neutrality.[250]

The Ti_4O_4 framework of $[\{TiOCl(O_2CCMe_3)THF\}_4]$ is depicted in Figure 3.7.

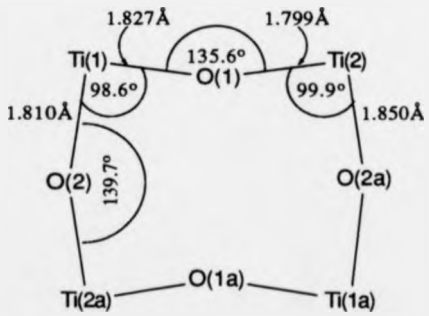


Figure 3.7 The Ti_4O_4 framework of $[\{TiOCl(O_2CCMe_3)THF\}_4]$

The bond angle Ti(1)-O(1)-Ti(2) of 135.6° is only slightly smaller than that found in the structural unit in *1* (137.3°), *2* (138.3°) and *3* (138.8°). As discussed previously for these latter three compounds, the angle Ti(1)-O(1)-Ti(2) deviates from 180° as a consequence of the presence of the two trimethylacetate ligands supporting the oxo bridge. The oxo ligands O(2) and O(2a) subtend an angle of 139.7° which is smaller than the analogous angle of the compound $[\{TaOCl_2(O_2CC_6H_4Me\text{-}p)\}_4]$ of 152°.[250]

The $Ti\text{-}O_{oxo}$ bond lengths are such that the oxo bridges are slightly unsymmetrical, the unsupported bridge having bond lengths of 1.810 and 1.850Å and the carboxylate supported oxo bridge having lengths of 1.827 and 1.799Å. These μ-oxo bridges are *cis* orientated to each other.

Titanium compounds containing the Ti_4O_4 cyclic core mainly occur in organometallic systems. These molecules contain four co-ordinate titanium ligands with the Ti_4O_4 ring in a near planar configuration having almost symmetrical Ti-O-Ti bridges. Compounds of this type include $[\{(\eta^5\text{-}C_5H_4(SiMe_3))Ti(\mu_2\text{-}O)(NCS)\}_4]$[237] and $[\{(\eta^5\text{-}C_5Me_5)TiOBr\}_4]$[214].

However, for six co-ordinate titanium complexes such as $[(NH_4)_2][TiO(C_2O_4)_2.H_2O]$[224] and $Cs_4[\{TiO(C_6H_6NO_6)\}_4.6H_2O]$[225] puckered eight membered ring are formed which have alternating shorter and longer bonds (1.74Å and 1.90Å for $Cs_4[\{TiO(C_6H_6NO_6)\}_4.6H_2O]$). Therefore, the constraints of the eight membered ring appear to be more favoured for four co-ordinate complexes over six co-ordinate species due to the bond angles around the titanium in the latter species not being ideal for a *cis* arrangement of the bridging oxygen atoms. However with a co-ordination number of four, the angles around the titanium atom are larger and can therefore support the ring structure without imposing more strain on the system. The strain is shown in the compound $[\{TiOCl(O_2CCMe_3)THF\}_4]$ with the opening up of the angles O(2)-Ti(1)-O(1) and O(2a)-Ti(2)-O(1) to 98.6 and 99.6° respectively from the ideal 90°.

Again, as has been seen with the species *1*, *2*, and *3* the co-ordinating ligand, in this case THF, is *trans* to the bridging oxygen of the supported unit. The average $Ti\text{-}O_{THF}$ bond length of 2.159Å is the longest of the average Ti-O distances which are graduated as $Ti\text{-}O_{acid\ anion}$ (2.071Å) > $Ti\text{-}\mu_2\text{-}O_{unsupported}$ (1.830Å) > $Ti_2\text{-}\mu_2\text{-}O_{supported}$ (1.813Å) thus indicating the relative strengths of the Ti-O bonds and also the π character of the Ti-O-Ti bridges.

The average carboxylate angles O-C-O are 125.0 and 123.8° which again reflect the strain within the molecule, due to deviations of many of the angles from the ideal. The

bridging carboxylate ligands are however symmetrically bridging which supports the observations drawn from the IR spectrum.

The terminal Ti-Cl average bond length of 2.319Å is only slightly larger those in *1* (2.288Å), *2* (2.262Å) and *3* (2.25Å).

3.6.8. Possible Routes to the Formation of [{TiOCl(O_2CCMe_3)THF}$_4$]

From initial hydrolysis experiments, [{$TiCl_2(O_2CCMe_3)THF\}_2O$] does not appear to give the tetranuclear species, but instead forms an oil which is a mixture of unidentifiable compounds. This reaction needs to be investigated more thoroughly, as there would seem to be no obvious reason why the hydrolysis reaction shown in the equation below, should not occur. Perhaps experimenting with a wider range of solvents and precipitation methods would enable a crystalline product to be isolated.

$$2[\{TiCl_2(O_2CCMe_3)THF\}_2O] + 2H_2O \longrightarrow [\{TiOCl(O_2CCMe_3)THF\}_4] + 4HCl$$

It may be possible that the reaction is a two stage process which could proceed according to the following two equations.

Route 1

$$2[\{TiCl_2(O_2CCMe_3)(Me_3CCO_2H)\}_2O] + 2H_2O \longrightarrow [\{TiOCl(O_2CCMe_3)(Me_3CCO_2H)\}_4] + 4HCl$$

Then

$$[\{TiOCl(O_2CCMe_3)(Me_3CCO_2H)\}_4] + 4\ THF \longrightarrow [\{TiOCl(O_2CCMe_3)THF\}_4] + 4\ Me_3CCO_2H$$

It would be interesting to carry out investigations by following the route of the above reactions by spectroscopic methods and isolating the product at each step, and then repeating the procedure for the following route.

Route 2

$$[\{TiCl_2(O_2CCMe_3)(Me_3CCO_2H)\}_2O] + 2THF \longrightarrow [\{TiCl_2(O_2CCMe_3)THF\}_2O] + 4Me_3CCO_2H$$

Then

$$2[\{TiCl_2(O_2CCMe_3)THF\}_2O] + 2H_2O \longrightarrow [\{TiOCl(O_2CCMe_3)THF\}_4] + 4HCl$$

This may enable some information concerning the hydrolysis reaction to be gained, but it seems most likely that the same product can be achieved through either route with careful consideration of the solvents used and the hydrolysis conditions.

CHAPTER FOUR

FURTHER OXO SPECIES OF THE ALKYL ACIDS

4. INTRODUCTION

Further oxo species of the alkyl acids have been prepared for this thesis by raising the reaction temperature. Previously reported species which are relevant to these new products will now be discussed.

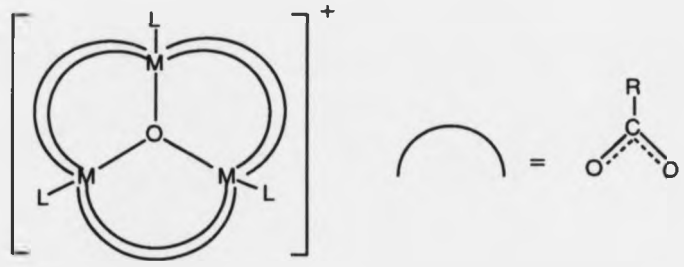
4.1. The μ_3-Oxo Bridge in Metal Complexes

Three-connected oxide ligands are found in a variety of metal complexes.[196] The μ_3-O unit is, in general, symmetrical, with essentially equal M-O distances, but may be planar or pyramidal. In the latter case the oxygen behaves as a 'capping' ligand and lies above a metal-metal bonded cluster of metal atoms, as represented below.

Planar Pyramidal 'capping'

Generally, the metal atoms are additionally linked by μ_2-bridging ligands such as hydroxy or carboxylate ligands.

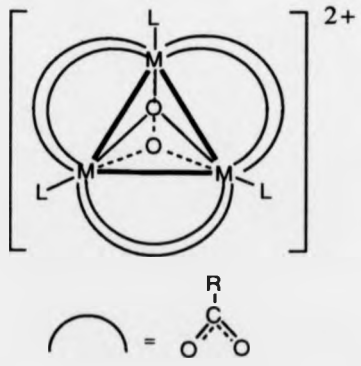
The planar trinuclear oxo structure of D_{3h} symmetry is structurally well-established as the central unit in a series of carboxylate bridge ions of general formula $[M_3(\mu_3\text{-}O)(O_2CR)_6L_3]^+$ (M=trivalent metal e.g. Fe^{III}, Mn^{III}, Cr^{III}, V^{III}, Co^{III}; R=generally Me, but a variety of others have been prepared; L=H_2O, THF, alcohols, pyridine or substituted pyridines).[111,251] The oxygen atom is located at the centre of an equilateral triangle of metal atoms. Two carboxylate groups bridge each pair of metal atoms, and a monodentate ligand is co-ordinated to each metal atom to give each of these an octahedral configuration, as shown in **(4.1)**.



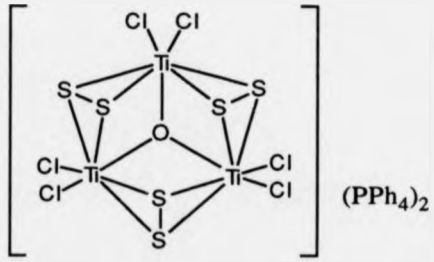
(4.1)

Some examples of this type of metal carboxylate species are $[\{Cr_3(\mu_3\text{-}O)(O_2CMe)_6(H_2O)_3\}Cl.6H_2O]$,[252] $[\{Fe_3(\mu_3\text{-}O)(O_2CCMe_3)_6(MeOH)_3\}Cl]$[253] and $[\{V_3(\mu_3\text{-}O)(O_2CCH_2Cl)_6(H_2O)_3\}(ClO_4)]$.[254] Mixed metal units for example Fe_2CrO and mixed oxidation states e.g. $Cr^{II}Cr_2^{III}O$ are also known.

A distinct group of complexes derived from molybdenum, tungsten and niobium has a similar molecular formula to that of the trinuclear oxo centred carboxylates discussed *viz.* $[M_3(\mu_3\text{-}O)_2(O_2CR)_6L_3]^{2+}$ **(4.2)** which have a different structure.



(4.2)



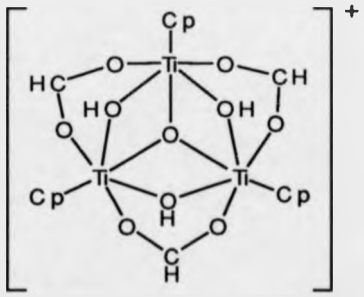
(4.3)

The structure is based on a metal-metal bonded equilateral triangle of metal atoms with an oxygen placed above the triangle, bonding to all three metal atoms. A second oxygen may then occupy the analogous μ_3-O bridging position on the opposite side of the metal triangle. Two carboxylate groups bridge each pair of metal atoms and ligands such as water or THF are terminally co-ordinated to the metals. Some

examples of these species are $[Mo_3(\mu_3\text{-}O)_2(O_2CMe)_6(H_2O)_3][CF_3SO_3]_2$,[255] $[W_3(\mu_3\text{-}O)_2(O_2CMe)_6(H_2O)_3][CF_3SO_3]_2$[256] and the compound $[Nb_3(\mu_3\text{-}O)_2(O_2CCMe_3)_6(THF)_3][BPh_4]$.[257]

Although not a titanium carboxylate, bis(tetraphenylphosphonium)hexachloro(μ-oxo)-tris(μ-disulfido)-tri-titanium(IV) **(4.3)** contains a pyramidal titanium μ_3-oxo core where the Ti-O-Ti angles range from 110.9 to 112.2°. The titanium atoms are linked by disulphido groups and the terminal ligands are chlorine atoms.[258]

Another bridging ligand is the hydroxo group as in the compound $[\{(\eta^5\text{-}Cp)_3Ti_3(\mu_3\text{-}O)(\mu_2\text{-}OH)_3(\mu_2\text{-}O_2CH)_3\}^+HCOO^-.2HCOOH]$.[234] Döppert and Thewalt have prepared this compound by hydrolysis of dicyclopentadienyltitanium(IV) dichloride in water at pH>5 and the subsequent reaction with formic acid. The structure of $[\{(\eta^5\text{-}Cp)_3Ti_3(\mu_3\text{-}O)(\mu_2\text{-}OH)_3(\mu_2\text{-}O_2CH)_3\}^+HCOO^-.2HCOOH]$ has been determined by X-ray analysis. The complex cation **(4.4)** is oxygen centred, with the three titanium atoms being additionally linked by hydroxo and formate bridges, with the co-ordination octahedra around each titanium atom completed by a η^5-bonded cyclopentadienyl group.



Average bond lengths:

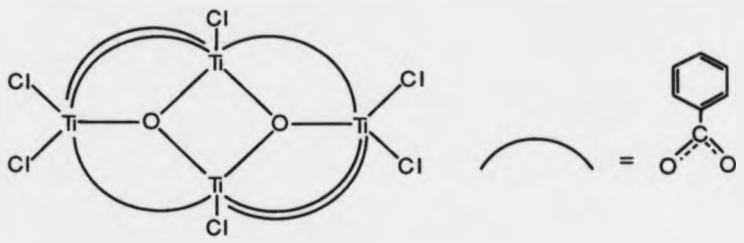
$Ti\text{-}O_{oxo}$	1.97Å
$Ti\text{-}O_{carboxylate}$	2.092Å
$Ti\text{-}O_{hydroxo}$	2.014Å
O-C-O	127.1Å

(4.4)

Examples of compounds containing two linked M_3O units to give a M_4O_2 core can be found for such elements as uranium, aluminium and iron.

4.2. The Reaction of $TiCl_4$ with Carboxylic Acids at Elevated Temperatures

The first example of a Ti_4O_2 core was reported by these laboratories in 1992. The compound $[Ti_4(\mu_3\text{-}O)_2Cl_6(\mu_2\text{-}O_2CPh)_6]$ **(4.5)** may be prepared in high yield by the action of benzoic acid on titanium tetrachloride at high temperatures (100-150°C).[191]



(4.5)

In view of the high yield 99%, the reaction was proposed to proceed simply, along the pathway shown by the equation below, with acid chloride also being obtained as a by-product, and a carboxylate anion providing both the oxo and acyl groups.

$$4TiCl_4 + 8PhCO_2H \longrightarrow [Ti_4(\mu_3\text{-}O)_2Cl_6(\mu_2\text{-}O_2CPh)_6] + 8HCl + 2PhCOCl$$

The titanium atoms are linked by both μ_3-oxo bridges and benzoate groups, with terminal chlorine atoms to give an overall distorted octahedral co-ordination of the titanium atoms.

The IR spectrum of this tetranuclear species showed carboxylate absorption bands which could be attributed to $\upsilon(COO)_{asym}$ and $\upsilon(COO)_{sym}$ at 1540 and 1405cm^{-1} respectively. Thus the Δ value is 135cm^{-1} which is in accord with the benzoate ligands adopting a symmetrical bridging co-ordination mode. The υ(Ti-O) of the Ti_4O_2 metal-oxo core was assigned to a band at 840cm^{-1}.

Similar high temperature reactions were carried out with various substituted benzoic acids in order to try to determine how the steric bulk and inductive effect of the substitutent affected the final structure and stoichiometry of the carboxylate. It was found that other acids yield compounds of different stoichiometry, as shown in Table 4.1.

Table 4.1 Products of the high temperature reaction of $TiCl_4$ with carboxylic acids.[188]

Carboxylic acid	Product
$PhCO_2H$	$[Ti_4O_2Cl_6(O_2CPh)_6]$
p-$XC_6H_4CO_2H$ X=F, Cl, Br, I	$[Ti_3O_2Cl_3(O_2CC_6H_4X\text{-}p)_5]$
p-$RC_6H_4CO_2H$ R=Me, Et, ^{i}Pr	$[Ti_3O_2Cl_3(O_2CC_6H_4R\text{-}p)_5]$
p-$Me_3CC_6H_4CO_2H$	$[\{TiCl(O_2CC_6H_4CMe_3\text{-}p)_2\}_2O]$
Me_3CCO_2H	$[\{TiCl(O_2CCMe_3)_2\}_2O]$
o-$MeC_6H_4CO_2H$	$[Ti_4O_2Cl_5(O_2CC_6H_4Me\text{-}o)_7]$
o-,*m*-$ClC_6H_4CO_2H$	$[Ti_3O_2Cl_4(O_2CC_6H_4Cl\text{-}o,\text{-}m)_4]$

Clearly, some slight variations in the reactant stoichiometry are required for the preparation of the titanium oxo species in Table 4.1. Overall, optimum yields are obtained when a molar ratio of near 1 : 2.5 ($TiCl_4$: acid) is utilised, the addition of further carboxylic acid simply resulting in unreacted acid remaining in the reaction solution after heating.

The *para*-substituted benzoic acids when heated to 100°C in 100-120°C petroleum ether gave compounds of the general formula $[Ti_3O_2Cl_3(O_2CR)_5]$. The *para*-toluate derivative $[Ti_3O_2Cl_3(O_2CC_6H_4Me\text{-}p)_5]$ gives a quantitative yield for the reaction expressed by the equation below.[192]

$$3TiCl_4 + 7p\text{-}MeC_6H_4CO_2H \xrightarrow{100\text{-}120^oC} [Ti_3O_2Cl_3(O_2CC_6H_4Me\text{-}p)_5] + 7HCl + 2p\text{-}MeC_6H_4COCl$$

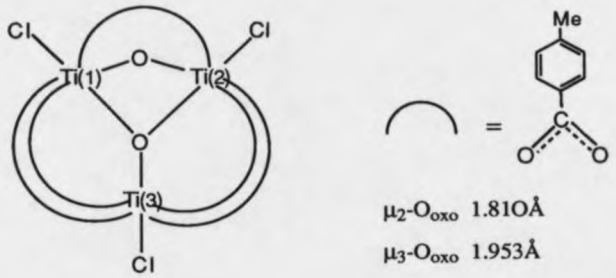
The IR spectrum of the mother liquor for this reaction indicated the presence of acid chloride and it again therefore appears that the carboxylic acid has a triple role to play in that it provides

(i) a proton for the HCl formation

(ii) an acyl group which removes further chlorines as RCOCl and

(iii) a remaining oxygen atom which contributes to the metal oxo cluster.

An X-ray structural study of $[Ti_3O_2Cl_3(O_2CC_6H_4Me\text{-}p)_5]$ **(4.6)** revealed the presence of both μ_3-O and μ_2-O units to give a $[Ti_3(\mu_2\text{-}O)(\mu_3\text{-}O)]^{8+}$ core.



(4.6)

One unique carboxylate group bridges Ti(1) and Ti(2), and the four carboxylates form two sets of bridging groups between Ti(2) and Ti(3) and Ti(1) and Ti(3). the inequivalence between these two sets, as indicated by the NMR data, arises from the overall configuration of the molecule and will be discussed later in this chapter. The compound shows structural similarities to the tris-chloromonopivalate [$TiCl_3(O_2CCMe_3)$] with μ_2-O and μ_3-O ligands taking the place of the bridging μ_2-Cl and μ_3-Cl and a further two carboxylate groups for neutrality.

While they do show some air reactivity associated with the presence of the Ti-Cl bonds, nevertheless, the overall stability of the oxo derivatives in Table 4.1 is demonstrated by the lack of further reaction when they are heated to 100-120°C in the presence of excess acid.

The *para*-substituted benzoic acid derivatives showed some similarities in their IR spectra, as displayed in Table 4.2.

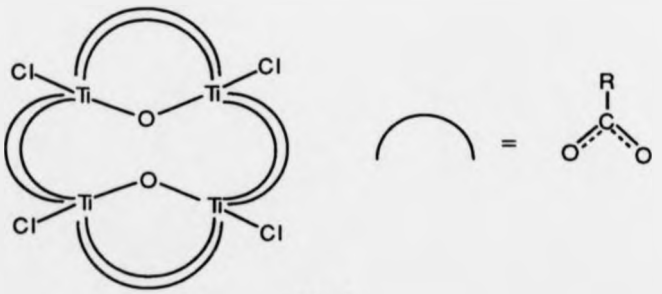
As can be seen from Table 4.2, the Δ values are in the range 125-160cm^{-1} which is consistent with the presence of bridging carboxylate groups. It is noteworthy that the more sterically hindered acids *p*-$Me_3CC_6H_4CO_2H$ and Me_3CCO_2H both, when reacted with $TiCl_4$ in a 1:2.5 ratio at temperatures of 100-120°C, produce compounds of the general formula [{$TiCl(O_2CR)_2$}$_2$O] according to the following equation.

$$2TiCl_4 + 5RCO_2H \longrightarrow [\{TiCl(O_2CR)_2\}_2O] + 5HCl + RCOCl$$
$$(R=p\text{-}Me_3CC_6H_4, CMe_3)$$

Table 4.2 Some pertinent IR data (cm^{-1}) for *para*-substituted benzoate complexes of the type $[Ti_3O_2Cl_3(O_2CR)_5]$.[188]

R	$\upsilon(COO)_{asym}$	$\upsilon(COO)_{sym}$	Δ	$\upsilon(Ti\text{-}O)_{bridge}$	$\upsilon(Ti\text{-}Cl)$
p-FC_6H_4	1550	1420	130	780	400, 380, 350
p-ClC_6H_4	1540	1410	130	780	450, 360, 340
p-BrC_6H_4	1540	1380	160	770	470, 430
p-IC_6H_4	1530	1400	130	765	460, 400, 350
p-MeC_6H_4	1535	1410	125	770	480, 400, 360
p-EtC_6H_4	1540	a	a	780	490, 370
p-$^iPrC_6H_4$	1540	a	a	780	370
[a] unassigned					

Although lacking direct structural evidence a structure **(4.7)** was postulated for compounds of the type $[\{TiCl(O_2CR)_2\}_2O]$ (R=*p*-$Me_3CC_6H_4$, CMe_3).[188]



(4.7)

However, work carried out for this thesis concerning R=CMe_3, suggests that due to the insolubility of the compound, $[\{TiCl(O_2CCMe_3)_2\}_2O]$ is polymeric in nature. This proposal will be discussed later in this chapter.

In addition to the aforementioned compounds, μ_3-O may act as a capping ligand. This is demonstrated in polyoxo- and polyoxochloro organometallic compounds of the type $[Ti_6(\mu_3\text{-}O)_4(\mu_3\text{-}Cl)_4L_6]$, $[Ti_6(\mu_3\text{-}O)_6(\mu_3\text{-}Cl)_2L_6]$ and $[Ti_6(\mu_3\text{-}O)_8L_6]$ (L=η^5-C_5H_5 or η^5-C_5H_4Me).[241]

4.3. RESULTS AND DISCUSSION

It is well known that $TiCl_4$ reacts with compounds containing protic hydrogens, such as alcohols, to eliminate HCl and produce a new compound, for example an alkoxide, as shown by the equation

$$TiCl_4 + 2EtOH \longrightarrow [TiCl_2(OEt)_2] + 2HCl$$

It is therefore surprising to find that the X-ray structures of $[\{TiCl_2(O_2CR)(RCO_2H)\}_2O]$ (R=Et, CMe_3) reveal that neutral carboxylic acid and chlorine ligands are situated on the same metal atom. It may be possible that further elimination of HCl could occur on heating as with $[Ti_2Cl_7(O_2CC_6H_4Cl\text{-}p)(p\text{-}ClC_6H_4CO_2H)]$ in the equation below, which was previously discussed in Chapter 2.

$$[Ti_2Cl_7(O_2CC_6H_4Cl\text{-}p)(p\text{-}ClC_6H_4CO_2H)] \xrightarrow{\text{solvent}} 2[TiCl_3(O_2CC_6H_4Cl\text{-}p)] + HCl$$

This section will therefore record the results of experiments carried out concerning the heating of the compounds $[\{TiCl_2(O_2CR)(RCO_2H)\}_2O]$ (R=Me, Et, CMe_3) in an attempt to produce new titanium carboxylate species *via* elimination of HCl.

4.3.1. Heating of the species $[\{TiCl_2(O_2CR)(RCO_2H)\}_2O]$ as a Synthesis of $[Ti_3O_2Cl_3(O_2CR)_5]$ (R=Et, CMe_3)

When the title compounds are heated to 40°C (R=CMe_3) or refluxed for 30 minutes in light petroleum (R=Et), white powders which analyse as $[Ti_3O_2Cl_3(O_2CR)_5]$ are obtained. These new compounds may be recrystallised from a dichloromethane-petroleum ether solution. An X-ray structural investigation of the propanoate derivative revealed a trinuclear species containing both (μ_2-O) and (μ_3-O) ligands. This structure is analogous to that of $[Ti_3O_2Cl_3(O_2CC_6H_4Me\text{-}p)_5]$ which has been discussed in the introduction to this chapter.[192] The high yields (R=Et, 85%; R=CMe_3, 80%) corresponding to the following equation , imply a straight conversion with the evolution of HCl, free carboxylic acid and acid chloride.

$$3[\{TiCl_2(O_2CR)(RCO_2H)\}_2O] \rightarrow 2[Ti_3O_2Cl_3(O_2CR)_5] + RCOCl + RCO_2H + 5HCl$$
$$(R=Et, CMe_3)$$

The carbonyl absorption bands of the acid chloride and free carboxylic acid can clearly be seen in the IR spectrum of the petroleum ether liquors which gives further evidence in favour of the above equation. Again, as we have seen previously, the production of acid chloride indicates the formation of an oxo bridge with the abstraction of an oxygen atom from a carboxylate ion. The products $[Ti_3O_2Cl_3(O_2CR)_5]$ (R=Et, CMe_3) may also be prepared by the reaction of $TiCl_4$ with the respective carboxylic acid with a 1:2.5 molar ratio of reactants utilising similar reaction conditions to those described above. Thus it has been found that compounds of the formulation $[\{TiCl_2(O_2CR)(RCO_2H)\}_2O]$ appear to be intermediates in the reaction of $TiCl_4$ with carboxylic acids at high temperature. It may therefore be possible that such intermediate species may be prepared with *para*-substituted benzoic acids which have also been shown to form the species $[Ti_3O_2Cl_3(O_2CR)_5]$ at elevated temperatures.

It is interesting to note that the ease of reaction of the species $[\{TiCl_2(O_2CR)(RCO_2H)\}_2O]$ on heating follows the order CMe_3>Et>>Me, since the trimethylacetate derivative reacts at 40°C, the propanoate derivative at 70°C, and the acetate derivative surprisingly remains unchanged, retaining the co-ordinated acid ligands.

As an important comparison, the species $[\{TiCl_2(O_2CR)THF\}_2O]$ (R=Me, Et, CMe_3) were also heated. In each case the compounds remained unchanged on refluxing in toluene solution (111°C) presumably due to the absence of any protic hydrogen atoms on the ligands which would enable elimination of HCl to occur. Further to this, there are no excess carboxylic acid ligands to enable the formation of an additional oxo bridge.

The compounds $[Ti_3O_2Cl_3(O_2CR)_5]$ (R=Et, CMe_3) were characterised by elemental analysis, and in addition, by their IR and ^1H NMR spectra, which will now be discussed.

IR Spectra of the compounds $[Ti_3O_2Cl_3(O_2CR)_5]$ (R=Et, CMe_3)

The IR spectra of the title species show two sets of carboxylate absorption bands between 1600 and 1400cm^{-1}. These bands are given in Table 4.3.

The values of Δ [$\upsilon(COO)_{asym}$-$\upsilon(COO)_{sym}$] of average 122cm^{-1} are indicative of bridging and / or chelating carboxylate bonding modes.

Table 4.3 Carboxylate absorption bands (cm^{-1}) of $[Ti_3O_2Cl_3(O_2CR)_5]$ (R=Et, CMe_3).

	$\upsilon(COO)_{asym}$	$\upsilon(COO)_{sym}$	Δ
R=Et	1561	1440	121
	1530	1407	123
R=CMe_3	1558	1427	131
	1522	1410	112

X-ray structure determination of the propanoate derivative has shown that the carboxylate ligands are symmetrically bridging, therefore confirming the use of the measure of Δ as a viable indication of the co-ordination mode of the carboxylate ligand.

The absorption bands of the [$Ti_3(\mu_3$-O)] and [$Ti_2(\mu_2$-O)] bridges are difficult to assign, but peaks at 715 and 645cm^{-1} (R=Et) and 716 and 665cm^{-1} (R=CMe_3) may be tentatively ascribed to these stretching vibrations.

Bands occurring at 450 and 340cm^{-1} (R=Et) and 475 and 355cm^{-1} (R=CMe_3) are assigned to terminal Ti-Cl stretching vibrations.

^1H NMR Spectra of the compounds $[Ti_3O_2Cl_3(O_2CR)_5]$ (R=Et, CMe_3)

The ^1H NMR spectrum of $[Ti_3O_2Cl_3(O_2CEt)_5]$ shows multiplets at δ2.62-2.45 (2H) and 1.33-1.11 (3H) which correspond to the methylene and methyl protons respectively of the carboxylate ligand. No hydroxyl proton signal is present in the NMR spectrum as would be expected.

The spectrum of the trimethylacetate derivative shows the interesting feature of three singlets at δ1.28, 1.25 and 1.20 with relative intensities of 2:2:1 respectively, as shown in Figure 4.1.

Peaks	Frequency	δ	Width (Hz)	Width (ppm)	Intensity	Area
1	320.68	1.2820	0.63	0.0025	27309.34	142.76
2	313.67	1.2540	0.63	0.0025	28678.19	149.39
3	300.82	1.2026	0.53	0.0021	15481.98	68.29

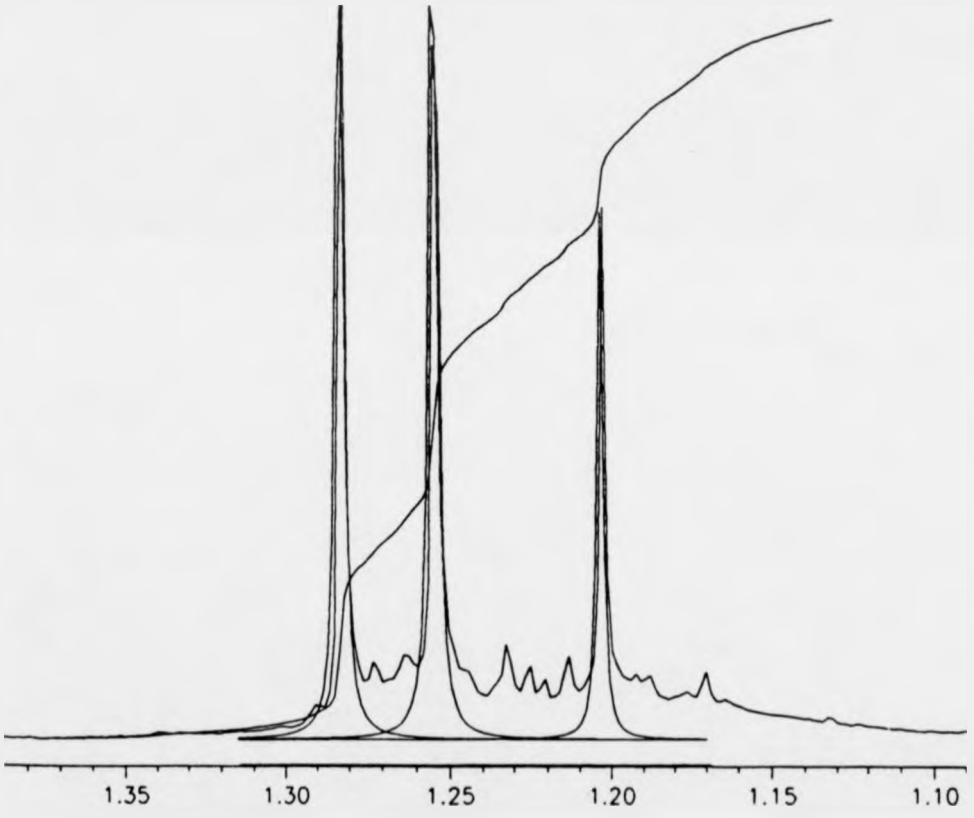


Figure 4.1 Methyl resonances in the ^1H NMR spectrum of $[Ti_3O_2Cl_3(O_2CCMe_3)_5]$ indicating three different spatially orientated trimethylacetate ligands in the molecule.

These signals correspond to the inequivalence of the five carboxylate ligands in the metal complex. This grouping of singlets has been witnessed previously in the ^{1}H NMR spectrum of the *p*-toluate derivative $[Ti_3O_2Cl_3(O_2CC_6H_4Me\text{-}p)_5]$.[192] Although not perfectly symmetrical, the latter compound has an approximate mirror plane leading to inequivalence of the carboxylate ligands which is seen in the *p*-methyl signals as a 2:2:1 ratio indicating three different types of carboxylate groups i.e. two sets of two and one unique carboxylate.

The ^{1}H NMR data of the trimethylacetate derivative clearly indicates that an analogous structure, Figure 4.2, to that of $[Ti_3O_2Cl_3(O_2CC_6H_4Me\text{-}p)_5]$ may be proposed. The carboxylate ratio of 2:2:1 is observed less clearly in the NMR spectrum of the propanoate derivative due the triplet and quartet signals occuring for the methyl and methylene moieties respectively and thus the signals appear as multiplets.

These results are further confirmed by the X-ray structural determination of $[Ti_3O_2Cl_3(O_2CEt)_5]$.

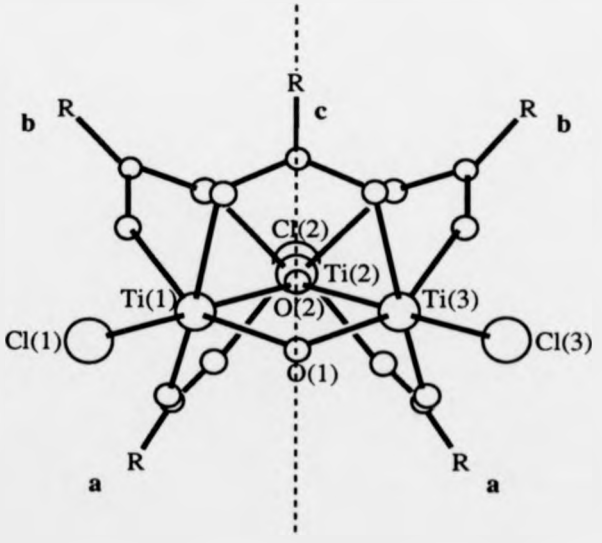


Figure 4.2 The proposed approximate mirror plane (dashed line) in $[Ti_3O_2Cl_3(O_2CR)_5]$ (R=Et, CMe_3) showing the three spatially different types of carboxylate ligands labelled a, b and c.

4.3.2. The X-Ray Crystal Structure of $[Ti_3O_2Cl_3(O_2CEt)_5]$

Crystals suitable for X-ray diffraction were obtained from a dichloromethane-hexane solution as colourless blocks. The structure of $[Ti_3O_2Cl_3(O_2CEt)_5]$ is shown in Figure 4.3 and selected bond lengths and angles are displayed in Tables 4.4 and 4.5 respectively.

The compound is isostructural with that of $[Ti_3O_2Cl_3(O_2CC_6H_4Me\text{-}p)_5]$ and contains three titanium atoms which are linked by μ_3-O and μ_2-O bridges, and additionally joined by five propanoate ligands.[192] The titanium atoms are in distorted octahedral environments and each is co-ordinated by five oxygen and one chlorine atoms.

The bond angles and lengths of the metal-oxo framework in $[Ti_3O_2Cl_3(O_2CEt)_5]$ are diagramatically displayed in Figure 4.4.

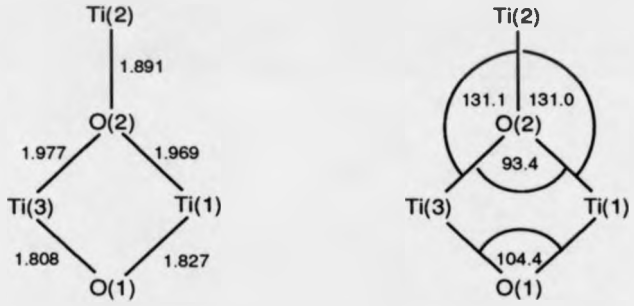


Figure 4.4 The metal oxo core in $[Ti_3O_2Cl_3(O_2CEt)_5]$ (Angles in degrees (°) and bond lengths in Angstroms Å)

The average Ti-μ_3-O distance of 1.946Å is very close to that found in the analogous *p*-methyl benzoate derivative $[Ti_3O_2Cl_3(O_2CC_6H_4Me\text{-}p)_5]$ of 1.953Å,[192] and the tetranuclear species $[Ti_4O_2Cl_6(O_2CPh)_6]$ of 1.961Å.[191] It can be seen from Figure 4.4 that there is a slight inequivalence in the Ti-O(2) bond lengths as would be expected with the presence of an additional Ti-μ_2-O bridge due to the inequivalence of electron density in the Ti-O(2) bonds.

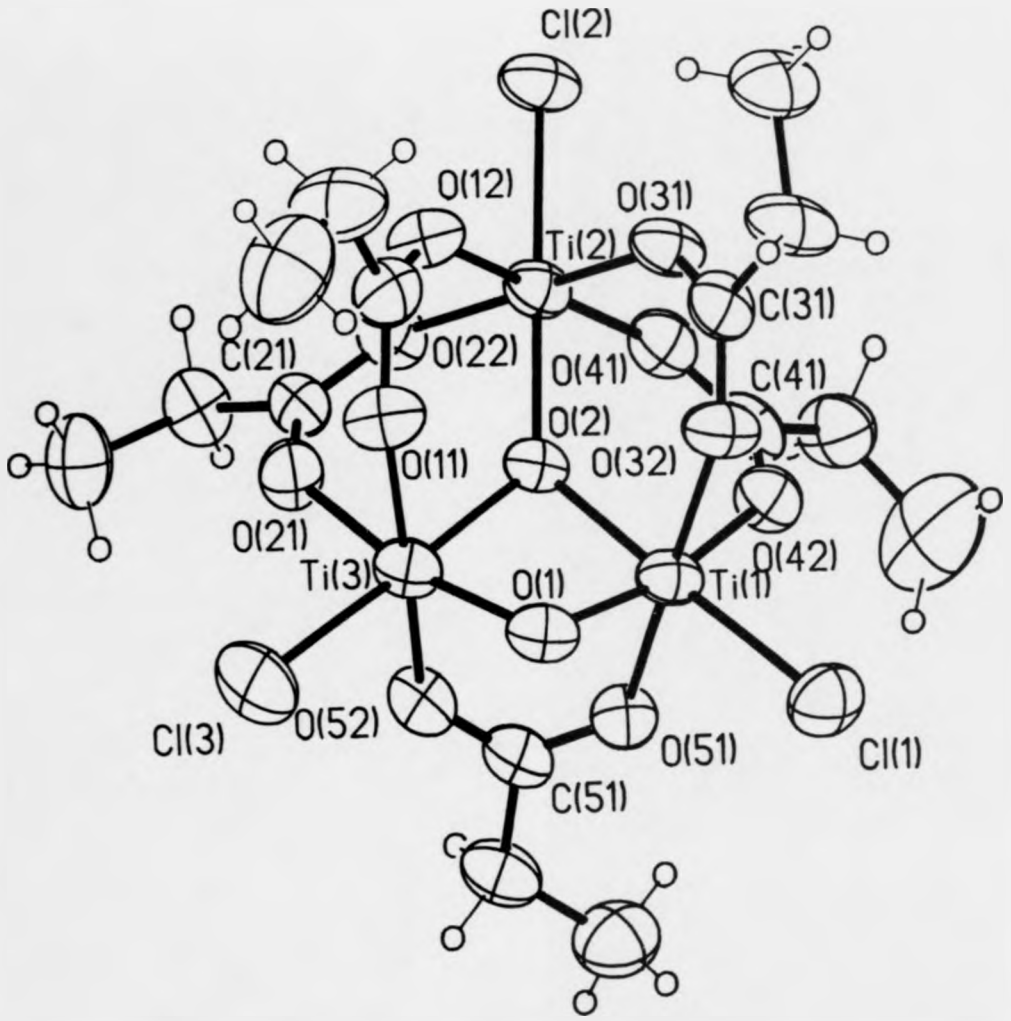


Figure 4.3 The X-ray crystal structure of $[Ti_3O_2Cl_3(O_2CEt)_5]$

Table 4.4 Selected bond lengths for $[Ti_3O_2Cl_3(O_2CEt)_5]$ (Å)

Ti(1)-Ti(3)	2.872(2)	Ti(1)-Cl(1)	2.269(2)
Ti(1)-O(1)	1.827(4)	Ti(1)-O(2)	1.969(4)
Ti(1)-O(32)	1.984(5)	Ti(1)-O(42)	2.020(4)
Ti(1)-O(51)	2.017(4)	Ti(2)-Cl(2)	2.287(2)
Ti(2)-O(2)	1.891(4)	Ti(2)-O(12)	2.013(5)
Ti(2)-O(22)	1.952(5)	Ti(2)-O(31)	1.995(5)
Ti(2)-O(41)	1.931(5)	Ti(3)-Cl(3)	2.271(2)
Ti(3)-O(1)	1.808(4)	Ti(3)-O(2)	1.977(4)
Ti(3)-O(11)	1.982(5)	Ti(3)-O(21)	2.035(4)
Ti(3)-O(52)	1.970(5)	O(11)-C(11)	1.268(8)
O(12)-C(11)	1.264(9)	O(21)-C(21)	1.261(7)
O(22)-C(21)	1.261(8)	O(31)-C(31)	1.249(8)
O(32)-C(31)	1.270(8)	O(41)-C(41)	1.283(8)
O(42)-C(41)	1.249(8)	O(51)-C(51)	1.267(8)
O(52)-C(51)	1.263(8)		

Table 4.5 Selected bond angles for $[Ti_3O_2Cl_3(O_2CEt)_5]$ (°)

Cl(1)-Ti(1)-O(1)	100.5(1)	Cl(1)-Ti(1)-O(2)	177.6(1)
O(1)-Ti(1)-O(2)	79.5(2)	Cl(1)-Ti(1)-O(32)	89.6(1)
O(1)-Ti(1)-O(32)	97.2(2)	O(2)-Ti(1)-O(32)	88.1(2)
Cl(1)-Ti(1)-O(42)	95.8(1)	O(1)-Ti(1)-O(42)	162.6(2)
O(2)-Ti(1)-O(42)	84.5(2)	O(32)-Ti(1)-O(42)	88.9(2)
Cl(1)-Ti(1)-O(51)	92.8(1)	O(1)-Ti(1)-O(51)	88.3(2)
O(2)-Ti(1)-O(51)	89.6(2)	O(32)-Ti(1)-O(51)	173.5(2)
O(42)-Ti(1)-O(51)	84.9(2)	Cl(2)-Ti(2)-O(2)	177.6(1)
Cl(2)-Ti(2)-O(12)	92.8(1)	O(2)-Ti(2)-O(12)	89.1(2)
Cl(2)-Ti(2)-O(22)	91.5(1)	O(2)-Ti(2)-O(22)	87.1(2)
O(12)-Ti(2)-O(22)	88.1(2)	Cl(2)-Ti(2)-O(31)	92.5(1)
O(2)-Ti(2)-O(31)	89.2(2)	O(12)-Ti(2)-O(31)	82.7(2)
O(22)-Ti(2)-O(31)	170.1(2)	Cl(2)-Ti(2)-O(41)	90.8(1)
O(2)-Ti(2)-O(41)	87.5(2)	O(12)-Ti(2)-O(41)	171.3(2)
O(22)-Ti(2)-O(41)	99.7(2)	O(31)-Ti(2)-O(41)	89.3(2)
Cl(3)-Ti(3)-O(1)	101.6(1)	Cl(3)-Ti(3)-O(2)	178.7(1)
O(1)-Ti(3)-O(2)	79.7(2)	Cl(3)-Ti(3)-O(11)	91.9(2)
O(1)-Ti(3)-O(11)	96.4(2)	O(2)-Ti(3)-O(11)	87.7(2)
Cl(3)-Ti(3)-O(21)	94.1(1)	O(1)-Ti(3)-O(21)	163.9(2)
O(2)-Ti(3)-O(21)	84.7(2)	O(11)-Ti(3)-O(21)	87.0(2)
Cl(3)-Ti(3)-O(52)	91.5(1)	O(1)-Ti(3)-O(52)	90.4(2)
O(2)-Ti(3)-O(52)	88.7(2)	O(11)-Ti(3)-O(52)	171.6(2)
O(21)-Ti(3)-O(52)	85.1(2)	Ti(1)-O(1)-Ti(3)	104.4(2)
Ti(1)-O(2)-Ti(2)	131.0(2)	Ti(1)-O(2)-Ti(3)	93.4(2)
Ti(2)-O(2)-Ti(3)	131.1(2)	Ti(3)-O(11)-C(11)	133.2(4)
Ti(2)-O(12)-C(11)	136.7(4)	O(11)-C(11)-O(12)	123.0(6)
Ti(3)-O(21)-C(21)	137.4(4)	Ti(2)-O(22)-C(21)	132.3(4)
O(21)-C(21)-O(22)	123.1(6)	Ti(2)-O(31)-C(31)	137.6(4)
Ti(1)-O(32)-C(31)	132.4(4)	O(31)-C(31)-O(32)	124.4(6)
Ti(2)-O(41)-C(41)	133.4(4)	Ti(1)-O(42)-C(41)	138.6(4)
O(41)-C(41)-O(42)	122.5(6)	Ti(1)-O(51)-C(51)	127.5(4)
Ti(3)-O(52)-C(51)	128.6(4)	O(51)-C(51)-O(52)	122.4(6)

As a comparison, the titanium-oxygen core of the symmetrical cation $[Cp_3Ti_3(\mu_3\text{-}O)(\mu_2\text{-}O_2CMe)_3(\mu_2\text{-}OH)_3]^+$ is shown in Figure 4.5 in which the Ti-μ_3-O bond lengths are nearly equivalent, having an average value of 1.970Å.[234]

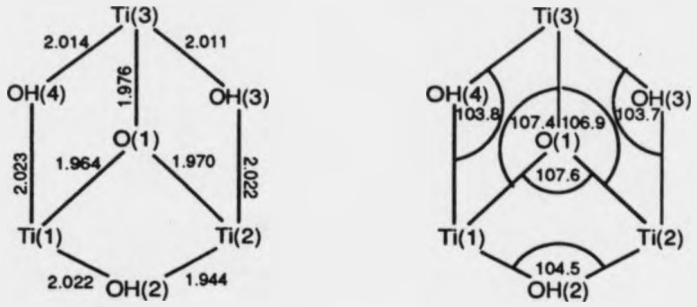


Figure 4.5 The metal oxo core in $[Cp_3Ti_3O(O_2CMe)_3(OH)_3]^+$ [Angles in degrees (°) and bond lengths in Angstroms Å].[234]

The average Ti-μ_2-O distance in $[Ti_3O_2Cl_3(O_2CEt)_5]$ is naturally shorter at 1.818Å which is in line with that found for $[Ti_3O_2Cl_3(O_2CC_6H_4Me\text{-}p)_5]$ of 1.810Å. Similar distances have been found previously in this thesis for Ti-μ_2-O linkages in the compounds $[\{TiCl(O_2CEt)(EtCO_2H)\}_2O]$ (1.794Å) and $[\{TiOCl(O_2CCMe_3)THF\}_4]$ (1.799-1.850Å).

The angles around the μ_3-oxygen total 355.5 and not 360°, indicating that the Ti_3-μ_3-O(2) core is not planar, and the oxygen is very slightly raised out of the plane. This can clearly be seen in Figure 4.6, which additionally shows the larger displacement of the μ_2-O(1) ligand, most probably caused by the constraints imposed by the bridging carboxylates.

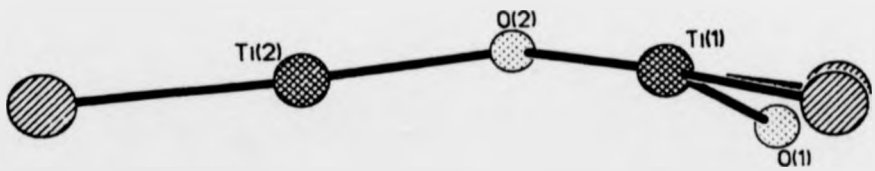


Figure 4.6 View of $[Ti_3O_2Cl_3(O_2CEt)_5]$ through the approximate plane of the titanium atoms showing the displacement of the bridging oxygens from planarity.

The O-C-O angles of the bridging propanoate groups are in the range 122.4-124.4° and have therefore opened up from the ideal 120°. There is some slight asymmetry in the lengths of each C-O carboxylate bond which was also found to occur in $[Ti_3O_2Cl_3(O_2CC_6H_4Me\text{-}p)_5]$. The asymmetry is not sufficiently noticeable in the IR spectrum of $[Ti_3O_2Cl_3(O_2CEt)_5]$ as the average value of Δ $[\upsilon(COO)_{asym})\text{-}\upsilon(COO)_{sym}]$ is 122cm^{-1}. Greater inequivalence, such as unidentate bonding causes an increase in Δ and is associated with values of Δ in excess of 200cm^{-1}.

The average terminal Ti-Cl distance in $[Ti_3O_2Cl_3(O_2CEt)_5]$ is similar to that of $[Ti_3O_2Cl_3(O_2CC_6H_4Me\text{-}p)_5]$ being 2.276 and 2.264Å respectively, and is in accord with the expected value for such bonds.

4.3.3. Preparation of the compound $[\{TiCl(O_2CCMe_3)_2\}_2O]$

Previous work by D. A. Brown in these laboratories concerning the high temperature reaction of titanium tetrachloride with trimethylacetic acid in a 1:2.5 molar ratio produced a colourless product which was formulated from elemental analysis as $[\{TiCl(O_2CCMe_3)_2\}_2O]$. The product was too insoluble for ^1H NMR experiments to be carried out but was further characterised by IR spectroscopy.[188]

$$2TiCl_4 + 5Me_3CCO_2H \longrightarrow [\{TiCl(O_2CCMe_3)_2\}_2O] + Me_3CCOCl + 5HCl$$

The IR spectrum of this compound showed absorption bands at 1550 and 1410cm^{-1} which were assigned as $\upsilon(COO)_{asym}$ and $\upsilon(COO)_{sym}$ respectively to give a Δ value of 140cm^{-1} which is consistent with the presence of bridging and / or bidentate chelating carboxylate groups. A large peak at 720cm^{-1} was assigned as υ(Ti-O) of the bridging metal oxygen framework. Although lacking direct structural evidence a structure was proposed for the compound $[\{TiCl(O_2CCMe_3)_2\}_2O]$ **(4.6)**.

Here for this thesis we report a similar product of empirical formula $[\{TiCl(O_2CCMe_3)_2\}_2]$ from the reaction of $TiCl_4$ with trimethylacetyl anhydride.

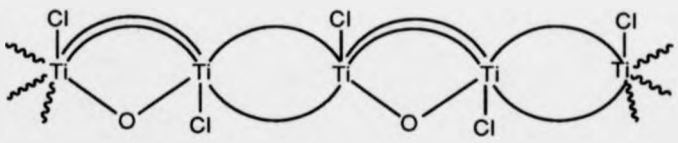
When $TiCl_4$ (1 mol) was added to a solution of trimethylacetyl anhydride (2.5 mol) in petroleum ether (100-120°) and heated to reflux for 3 hours, a white powder slowly precipitated. After cooling and filtering, the powder was isolated in 88% yield according to the equation.

$$2TiCl_4 + 5(Me_3CCO)_2O \longrightarrow [\{TiCl(O_2CCMe_3)_2\}_2O] + 6Me_3CCOCl$$

Trimethylacetyl chloride is a co-product of the above reaction and was observed in the IR spectrum of the petroleum ether reaction liquors.

In view of the very limited solubility in common organic solvents, it is assumed that the product is polymeric containing both bridging oxo and carboxylate groups. This is in contrast to the tetranuclear species previously proposed for a compound of similar stoichiometry. The existence of a polymeric rather than tetranuclear species is further supported by the knowledge of the solubility of compounds such as the tetramer $[\{TiOCl(O_2CCMe_3)THF\}_4]$ and the binuclear $[\{TiCl_2(O_2CCMe_3)(Me_3CCO_2H)\}_2O]$.

A polymeric structure such as that shown below may be postulated for $[\{TiCl(O_2CCMe_3)_2\}_2O]$.



IR Spectrum of $[\{TiCl(O_2CCMe_3)_2\}_2O]$

Four carboxylate absorption bands were assigned in the region 1600-1400cm^{-1} as shown in Table 4.6. The values of Δ of 80 and 135cm^{-1} are indicative of bridging and / or chelating carboxylic groups. The two sets of carboxylate values are most probably due to a lone bridging pair of carboxylate ligands and a μ_2-O supported pair of carboxylate ligands as is suggested in the proposed structure above.

Table 4.6 Carboxylate stretching vibrations (cm^{-1}) of the compound $[\{TiCl(O_2CCMe_3)_2\}_2O]$ in the IR.

$\upsilon(COO)_{asym}$	$\upsilon(COO)_{sym}$	Δ
1590	1510	80
1550	1413	137
$\Delta=\upsilon(COO)_{asym}-\upsilon(COO)_{sym}$		

Grigor'ev has previously proposed that Δ values for chelating carboxylates are less than Δ values for the bridging ligand. These proposals were based on the assumption that the O-C-O angle is smaller in chelating than in bridging acetates, and also on theoretical calculations which showed that decreasing the O-C-O angle subsequently decreases Δ.[129]

Therefore, as the value of $\Delta=80cm^{-1}$ is believed to be due to bridging carboxylates in the polymeric chain, it may possibly be assigned to the unsupported bridging ligands which may have a smaller O-C-O angle due to the lack of constraints being imposed by an additional oxo bridge.

The larger Δ value of $135cm^{-1}$ would correspond to the supported carboxylate bridge where the O-C-O angle would have opened up to about 122-125° as has been seen in $[\{TiCl_2(O_2CPh)(MeCO_2Et)\}_2O]$, $[\{TiCl_2(O_2CR)(RCO_2H)\}_2O]$ (R=Et, CMe_3) and $[\{TiCl_2(O_2CCH_2OC_6F_5)THF\}_2O]$. However these suggestions should be regarded as speculative since Deacon and Phillips have shown that for metal acetates low values of Δ are not necessarily associated with small O-C-O angles.[117]

A large band centred at $720cm^{-1}$ is assigned to υ(Ti-O-Ti) and resembles the similarly assigned bands in $[\{TiCl_2(O_2CR)(RCO_2H)\}_2O]$ and $[\{TiCl_2(O_2CR)THF\}_2O]$ (R=Me, Et, CMe_3).

Signals at 410, 390, 375 and $335cm^{-1}$ are assigned to υ(Ti-Cl) vibrations.

CHAPTER FIVE

ROOM TEMPERATURE REACTIONS OF $TiCl_4$ WITH THE ACIDS RCO_2H ($R=C_6F_5$, $CH_2C_6F_5$)

5. INTRODUCTION

Previously in Chapter 1, a brief overview of the preparation of titanium(IV) alkoxides was presented. In addition to these compounds a number of mixed titanium alkoxide-carboxylate species have been reportedly synthesised which will now be discussed.

5.1. Titanium Mixed Alkoxide and Carboxylate species

Titanium(IV) alkoxide-carboxylates are made generally by reacting the tetra-alkoxide with an appropriate amount of carboxylic acid. Compounds of this nature with the general formula $[Ti(O_2CC_6H_4OH\text{-}o)_2(O^iPr)_2]$, $[Ti(O_2CC_6H_4OH\text{-}o)_2(O^iPr)(O_2CR)]$ and $[Ti(O_2CC_6H_4OH\text{-}o)(O^iPr)(O_2CR)_2]$ (R=$C_{11}H_{23}$, $C_{15}H_{31}$ and $C_{21}H_{43}$) have been isolated.[259] The IR spectra of these species indicated that the carboxylate groups of the fatty acids were unidentate with the salicylate ligand in a bidentate co-ordination mode. These proposals however have not been confirmed by X-ray structure analysis.

The addition of $[Ti(OCHMe_2)_4]$ to a benzene solution of benzoic acid produces $[Ti(OCHMe_2)_3(O_2CPh)]$ after refluxing for 8 hours. The IR spectrum of the resultant colourless product exhibits absorption bands assigned to $\upsilon(COO)_{asym}$ and $\upsilon(COO)_{sym}$ at 1560 and 1420cm^{-1} respectively, thus giving a Δ value of 140cm^{-1} which would tend to indicate the presence of a symmetrical bridging or chelating benzoate group.[248]

Heterocyclic carboxylates of titanium(IV) of the type $[Ti(O^iPr)_{4-n}L_n]$ (n=1-3, HL=3-furancarboxylic acid) have been reported. $[Ti(O^iPr)L_3]$ was proposed to be dimeric with two bridging *iso*-propoxy ligands and three chelating carboxylate ligands on each titanium centre, thus giving the titanium atom a co-ordination number of eight.[260] However, in light of the information that now exists in this area, a seven co-ordinate monomeric structure similar to that of $[Cp^*Ti(O_2CPh)_3]$[133] may possibly exist.

The reactions of titanium alkoxides with aliphatic carboxylic acids have been investigated with a view to preparing the tetra-carboxylate derivatives $[Ti(O_2CR)_4]$.[261] Air sensitive mono- and dicarboxylate derivatives are produced quantitatively but complicated

side reactions ensue with the formation of the tricarboxylate derivatives, giving a mixture of $[TiO(O_2CR)_2]$ and $[Ti(OR)(O_2CR)_3]$. With benzoic acid, it was suggested that the reaction, after formation of the dicarboxylate derivative could proceed *via* the scheme outlined below.

$$[Ti(O_2CPh)_2(OR)_2] + PhCO_2H \xrightarrow{slow} [Ti(O_2CPh)_3(OR)] + ROH$$

$$[Ti(O_2CPh)_3(OR)] \longrightarrow [TiO(O_2CPh)_2] + PhCO_2R$$

(R=^{i}Pr, Et)

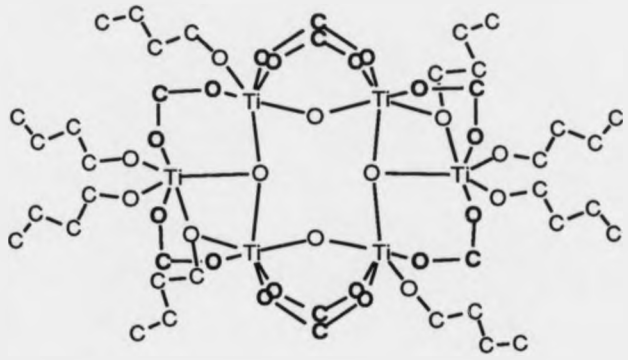
This final reaction was further confirmed by distilling out the corresponding esters of benzoic acid from the reaction liquor. $[TiO(O_2CPh)_2]$ was suggested to contain the titanyl moiety Ti=O. However, in view of the results obtained in this thesis it seems unlikely that a terminal oxygen is present and the compound most likely exists as a cyclic structure of the formulation $[TiO(O_2CPh)_2]_n$. The course of the reaction seems to be unaffected by excess carboxylic acid; even when the ratio of $[Ti(OR)_4]$ (R=Et, ^{i}Pr) to benzoic acid is greater than 1:4, the only product isolated is $[TiO(O_2CPh)_2]$.

5.2. Mixed Alkoxide and Carboxylate Oxo Titanium(IV) species

Mixed alkoxide and carboxylate oxo titanium species have also been prepared by a sol-gel route. The sol-gel process is based upon the polycondensation of metal alkoxides or other metal compounds to produce a molecular oxide network which offers a new approach to the synthesis of glasses and ceramics. A good detailed review of mixed metal oxides and metal alkoxide carboxylates as intermediates in sol-gel processes has recently been published by Hampden-Smith and co-workers.[262]

It has been shown that some of the most common additives, such as acetic acid or acetylacetone, may chemically react with alkoxides at a molecular level, giving rise to new molecular precursors and thus modifying the hydrolysis-condensation process. Better control of the process requires characterisation of the intermediate chemical species which are formed. One such intermediate is $[Ti_6(\mu_2\text{-}O)_2(\mu_3\text{-}O)_2(\mu_2\text{-}O^nBu)_2(O^nBu)_6(\mu_2\text{-}O_2CMe)_8]$ whose framework (**5.1**) is shown

below.[263] The compound is a hexanuclear hydrolysed derivative of titanium(IV) butoxide which is chemically modified by acetic acid.



(5.1)

This compound constitutes good structural reference for the study of the chemical modifications that occur in sol-gel processing and is prepared by mixing acetic acid with titanium tetra-butoxide in a 1:2 molar ratio. After a few days, transparent colourless crystals are formed which are air and moisture sensitive. The hexameric unit contains two triply bridging oxygen atoms, and two doubly bridging oxygen atoms. All the acetate ligands are bridging but two types of butoxy groups can be distinguished, namely six terminal and two bridging.

The main features of the IR spectrum of this compound are the bands associated with υ(C-O) of the butoxy groups at around 1000cm^{-1}, and the bands of $\upsilon(COO)_{asym}$ and $\upsilon(COO)_{sym}$ of the bridging acetate moiety in the region 1600-1400cm^{-1}. These latter absorption bands are displayed in Table 5.1. The crystal structure of the compound has revealed the presence of only one chemical type of acetate group which are all bridging two titanium atoms quite symmetrically, and therefore the presence of three asymmetric carboxylate stretching bands would not be expected. The authors suggest that the splitting of the asymmetric carboxylate band is a consequence of the variations of the O-C-O angle (121-123°) observed for the acetate groups.

Table 5.1 Carboxylate stretching frequencies (cm^{-1}) in the IR spectrum of $[Ti_6O_4(O^nBu)_8(O_2CMe)_8]$.[264]

$\upsilon(COO)_{asym}$	$\upsilon(COO)_{sym}$	Values of Δ
1600		155
1580	1445	135
1555		110

The Δ values $[\upsilon(COO)_{asym}-\upsilon(COO)_{sym}]$ of 110-155cm^{-1} are in agreement with the values proposed by Deacon and Phillips which suggest bridging acetate co-ordination. Unfortunately, absorption bands due to Ti-O-Ti bridging stretching vibrations were not assigned.

The strong reactivity of metal alkoxides is under the control of two main parameters; the electrophilic power of the metal atom and the degree of unsaturation of the metal. In the liquid state $[Ti(O^nBu)_4]$ is trimeric with five-fold co-ordinated metal atoms and therefore the full co-ordination of the titanium atom is not satisfied. One of the possible roles of the acetic acid is to increase the co-ordination number of the titanium atoms up to six. Further to this the acid reacts with butanol molecules to produce an ester and water, the water then hydrolysing the Ti-butoxy bonds leading to the Ti-O-Ti skeleton.

The formation of the compound $[Ti_6O_4(O^nBu)_8(O_2CMe)_8]$ can be schematised by the following chemical reactions.

$$6[Ti(O^nBu)_4] + 12MeCO_2H \longrightarrow [Ti_6(O^nBu)_{16}(O_2CMe)_8] + 8{}^nBuOH + 4MeCO_2H$$

The excess acetic acid then reacts with butanol to produce butyl acetate and water, the former of which has been identified and characterised by IR spectroscopy.

$$4{}^nBuOH + 4MeCO_2H \longrightarrow 4{}^nBuO_2CMe + 4H_2O$$

Hydrolysis of the butoxy-titanium bonds then occurs.

$$[Ti_6(O^nBu)_{16}(O_2CMe)_8] + 4H_2O \longrightarrow [Ti_6(OH)_4(O^nBu)_{12}(O_2CMe)_8] + 4^nBuOH$$

$$[Ti_6(OH)_4(O^nBu)_{12}(O_2CMe)_8] \longrightarrow [Ti_6O_4(O^nBu)_8(O_2CMe)_8] + 4^nBuOH$$

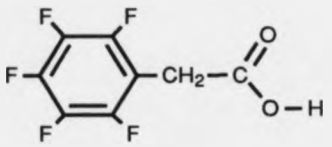
Thus, the overall reaction may be written as

$$2[Ti_3(O^nBu)_{12}] + 12MeCO_2H \longrightarrow [Ti_6O_4(O^nBu)_8(O_2CMe)_8] + 12^nBuOH + 4^nBuO_2CMe$$

A similar compound containing ethoxide ligands may be prepared by slowly evaporating a solution of $[Ti(OEt)_4]$ in glacial acetic acid and ethanol. The formation of the hexanuclear molecule $[Ti_6(\mu_2\text{-}O)_2(\mu_3\text{-}O)_2(\mu_2\text{-}OEt)_2(OEt)_6(\mu_2\text{-}O_2CMe)_8]$ again occurs through partial hydrolysis reactions of the titanium-ethoxide bonds.[264] The arrangement of the ligands around the titanium metal centres are identical to those found in the compound $[Ti_6O_4(O^nBu)_8(O_2CMe)_8]$ as discussed above. Unfortunately only a small number of crystals of the ethoxide-acetate species were produced and therefore it was not possible for IR spectral data to be collected. This would have proved a useful aid in the spectral characterisation of a similar alkoxide-carboxylate product which was unintentionally prepared whilst carrying out $TiCl_4$ and carboxylic acid reactions for this thesis. This next section will be given over to the preparation of the compound $[Ti_6(\mu_2\text{-}O)_2(\mu_3\text{-}O)_2Cl_2(\mu_2\text{-}OEt)_2(OEt)_4(\mu_2\text{-}O_2CH_2C_6F_5)_8]$ and discussion of its structural features.

5.3. Preparation of the compound $[Ti_6(\mu_2\text{-}O)_2(\mu_3\text{-}O)_2Cl_2(\mu_2\text{-}OEt)_2(OEt)_4(\mu_2\text{-}O_2CCH_2C_6F_5)_8]$

We have seen in Chapter 3 that pentafluorophenoxyacetic acid, a stronger acid than acetic, propanoic and trimethylacetic acids, produces $[\{TiCl_2(O_2CCH_2OC_6F_5)\}_2O]$ on reaction with $TiCl_4$. Continuing with the use of stronger carboxylic acids it was considered of interest to study the reaction of $TiCl_4$ with pentafluorophenylacetic acid **(5.2)** which does not contain an ethereal oxygen and therefore, unlike $C_6F_5OCH_2CO_2H$, does not have the ability to act as a terdentate donor ligand.



(5.2)

Initial experiments were concerned with the addition of $TiCl_4$ to pentafluorophenylacetic acid in a 1:2 molar ratio in chloroform at ambient temperature. On one occasion, a small number of crystals were deposited on the sides of the Schlenk tube, which enabled X-ray diffraction studies to be carried out on the product. It was of great surprise to discover that the product was a titanium oxo alkoxide-carboxylate species, as no alcohol had been intentionally added to the reaction mixture. The compound, of formulation $[Ti_6O_4Cl_2(OEt)_6(O_2CCH_2C_6F_5)_8]$, contains three types of bridging units; oxygen atoms, pentafluorophenylacetate ligands and ethoxide groups. This is in addition to terminal ethoxide and chlorine ligands. The ethanol, which must have been present during the reaction, was traced to the chloroform solvent which, instead of being stabilised with amylene, was of a grade which was stabilised with ethanol. This would of course lead to the reaction of $TiCl_4$ with both the carboxylic acid and the ethanol to eliminate HCl. Additionally, as has been discussed in the short introduction to this section, the alcohol has the ability to react with the carboxylic acid to generate an ester and water, the latter of which may attack either the Ti-Cl functionality or the Ti-O bonds of the alkoxide or carboxylate moieties to form oxo bridges which may link the titanium atoms to form small cluster molecules.

Thus, the addition of $TiCl_4$ (1 mol) to pentafluorophenylacetic acid (2 mol) in chloroform stabilised with ethanol produced a yellow solution from which, on addition of petroleum ether, a white powder was precipitated. The solid was washed with light petroleum and left in a petroleum solution for 3 days, within which time a small number of crystals were deposited. IR spectroscopy revealed that the bulk solid and the crystals were the same compound. Unfortunately, not enough product was prepared to enable elemental analysis and ^1H NMR spectroscopic measurements to be carried out. Further to this,

repeated efforts to recreate the product by using chloroform which was stabilised with ethanol, and chloroform with the addition of the stoichiometric amount of ethanol, failed. Only oils were able to be isolated which appeared to be mixtures from IR determinations. Therefore, the reaction conditions could not be reproduced effectively enough for $[Ti_6O_4Cl_2(OEt)_6(O_2CCH_2C_6F_5)_8]$ to be prepared again. Clearly this reaction should be investigated in more detail in order to prepare the titanium oxo alkoxide-carboxylate species in high yield and possibly determine the compounds which are intermediate in the formation of the hexameric product.

Before the addition of $TiCl_4$, the reaction mixture consists of pentafluorophenylacetic acid in chloroform with ethanol. Water would be generated by reaction of the carboxylic acid and the alcohol, as shown in the equation below, to produce ethyl pentafluorophenylacetate and water.

$$C_6F_5CH_2CO_2H + EtOH \longrightarrow C_6F_5CH_2CO_2Et + H_2O$$

On addition of $TiCl_4$, HCl may be eliminated by reaction with the protic hydrogens of the acid, the alcohol or the water. The ester which will be in the reaction mixture does not appear to take part in co-ordination to the metal centre, at least not in the final compound.

Thus, the overall reaction may be written as

$$6TiCl_4 + 12C_6F_5CH_2CO_2H + 10EtOH \longrightarrow [Ti_6O_4Cl_2(OEt)_6(O_2CCH_2C_6F_5)_8] + 4C_6F_5CH_2CO_2Et + 22HCl$$

It may be noted that although structurally comparable with $[Ti_6O_4(O^nBu)_8(O_2CMe)_8]$ and $[Ti_6O_4(OEt)_8(O_2CMe)_8]$, the compound $[Ti_6O_4Cl_2(OEt)_6(O_2CCH_2C_6F_5)_8]$ contains two terminal chlorine atoms indicating that possibly there was no more ethanol for reaction with the Ti-Cl bonds to form $[Ti_6O_4(OEt)_8(O_2CCH_2C_6F_5)_8]$. This area of titanium carboxylate chemistry could be studied in more detail, with the possibility of preparing products having differing alkoxide to chlorine ratios. Many factors may influence the stoichiometry of the final product, particularly the amount of time that the carboxylic acid and the alcohol are together in the reaction mixture prior to the addition of $TiCl_4$. A possible way of investigating this would be to mix the two components for different lengths of time

before the addition of $TiCl_4$ and then examine the products, but clearly the reaction conditions are very delicate and many side reactions could prevail.

IR Spectrum of $[Ti_6O_4Cl_2(OEt)_6(O_2CCH_2C_6F_5)_8]$

Absorption bands at 1600 and 1572cm^{-1} are assigned to $\upsilon(COO)_{asym}$ vibrations and $\upsilon(COO)_{sym}$ bands are labelled at 1434 and 1395cm^{-1}. This would therefore give Δ values of 166 and 177cm^{-1} which are in accord with bridging carboxylate Δ values which have been reviewed by Deacon and Phillips.[117]

$[Ti_6O_4Cl_2(OEt)_6(O_2CCH_2C_6F_5)_8]$ apparently shows two sets of carboxylate stretching bands in the IR. Although of not greatly differing magnitude, these may be a consequence of the slight asymmetry of some of the carboxylate ligands which is evident from the X-ray structure, and is a result of differing ligands *trans* to each of the co-ordinating oxygen atoms.

The carbon-oxygen stretching bands of the ethoxide ligands occur at 1115 and 1074cm^{-1}; the monodentate ethoxides having shorter C-O bond lengths are assigned to the band at 1115cm^{-1}, while the bridging ethoxide groups are assigned to the absorption band at 1074cm^{-1}.

The vibrations of the titanium-oxygen fragments containing μ_3- and μ_2-oxygen bridges are more difficult to assign but bands at 660 and 691cm^{-1} may possibly be due to the $Ti_3(\mu_3\text{-}O)$ and $Ti_2(\mu_2\text{-}O)$ vibrations respectively. Unfortunately IR spectra were not recorded in the 400-200cm^{-1} region and therefore no υ(Ti-Cl) bands are assigned.

5.3.1. X-Ray Crystal Structure of $[Ti_6O_4Cl_2(OEt)_6(O_2CCH_2C_6F_5)_8]$

The structure of $[Ti_6O_4Cl_2(OEt)_6(O_2CCH_2C_6F_5)_8]$ is shown in Figure 5.1, with the Ti_6O_4 core displayed in Figure 5.2. Selected bond lengths and angles are shown in Tables 5.2 and 5.3 respectively.

The compound contains a hexameric Ti_6 unit with a molecular formula of $[Ti_6O_4Cl_2(OEt)_6(O_2CCH_2C_6F_5)_8]$. Each titanium is six co-ordinate and in a near octahedral environment.

There are four oxygen atoms in bridging positions in the unit; two are triply bridging (μ_3-O) and two are doubly bridging (μ_2-O). Further, the titanium atoms are linked by pentafluorophenylacetate groups. Two types of ethoxy groups may be distinguished; four terminal and two bridging, and the remaining two co-ordination sites are occupied by chlorine atoms. As can be seen from Figure 5.2, each titanium atom is bonded to a triply bridging oxygen but only four of the titanium atoms are bonded to a doubly bridging oxygen.

In the different titanium octahedra, the bond lengths Ti-O vary from 1.714 to 2.107Å. The titanium-oxygen bonds of the terminal ethoxy groups are short, averaging 1.717Å. As a result of this strong bond to the titanium atom, the opposite Ti-μ_3-O bond is lengthened by the *trans* influence. In contrast, the Ti-O bonds of the bridging ethoxy group are 1.885 and 2.104Å due to some asymmetry in the bridging unit caused by differing *trans* ligands to each bond. The difference in the titanium-ethoxide distances as a function of the co-ordination scheme has also been noted in $[Ti_2Cl_4(\mu_2\text{-}OEt)_2(OEt)_2]$ where the Ti-O bond lengths are equal to 1.77 and 1.96Å for the monodentate and the bridging group respectively.[92]

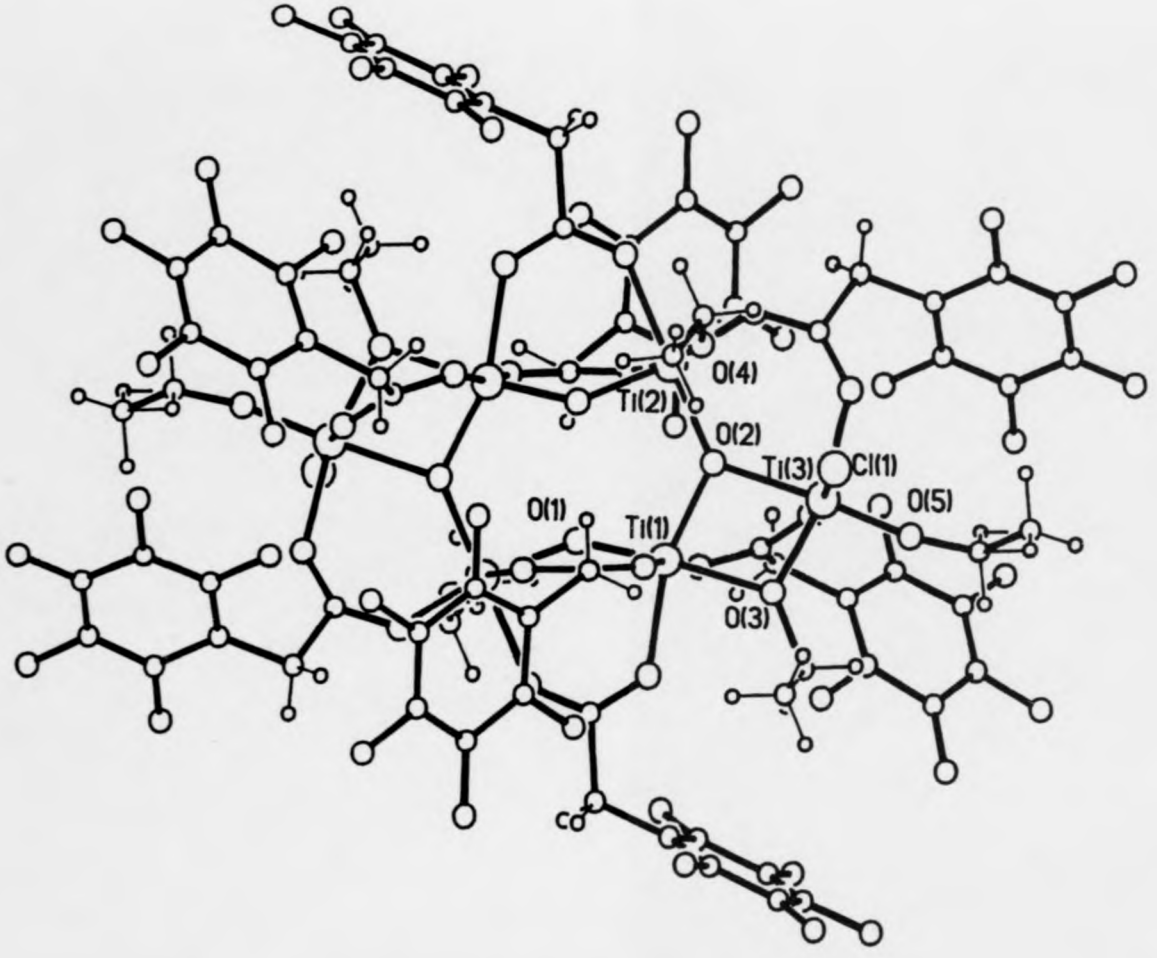


Figure 5.1 The X-ray crystal structure of $[Ti_6O_4Cl_2(OEt)_6(O_2CCH_2C_6F_5)_8]$

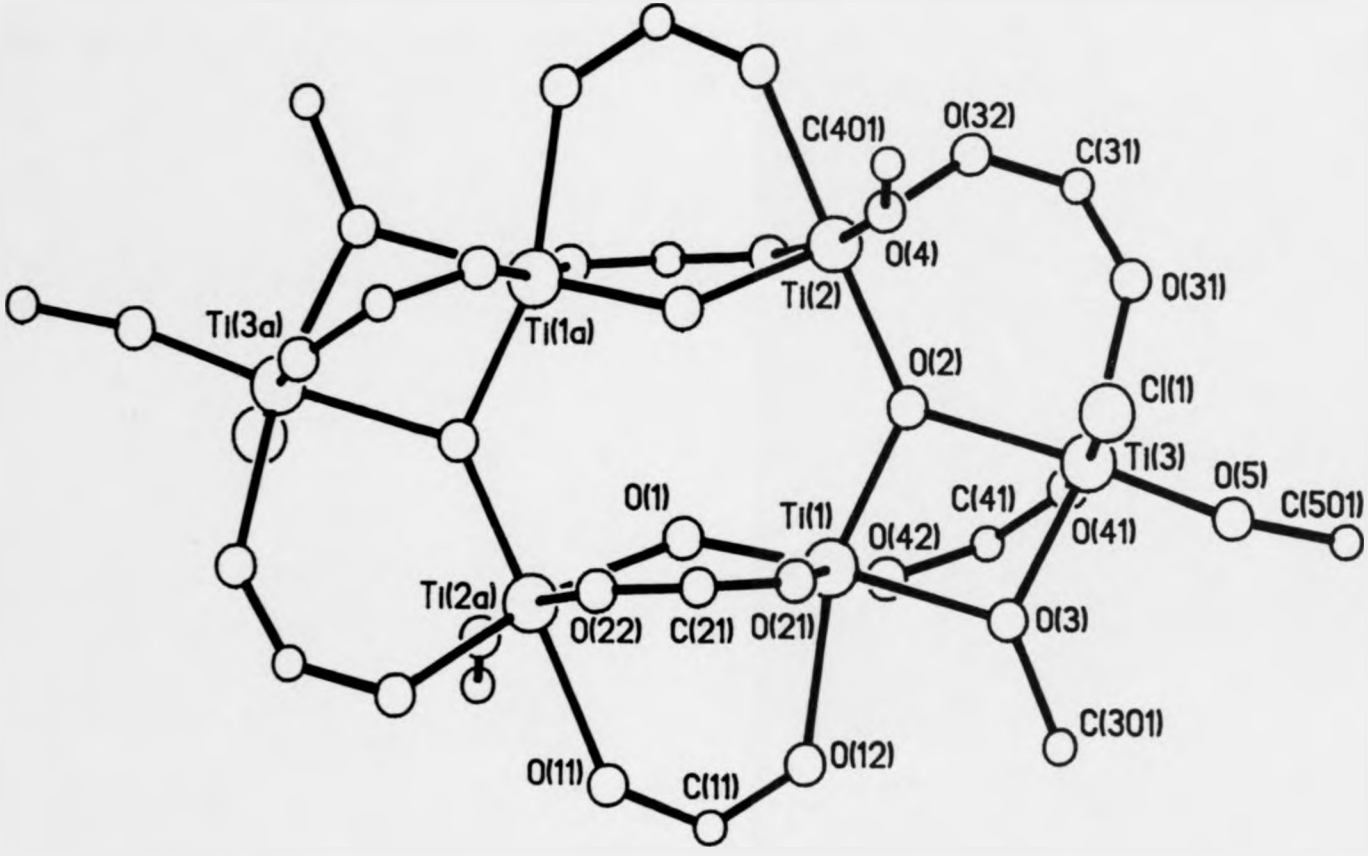


Figure 5.2 The structural core of the compound $[Ti_6O_4Cl_2(OEt)_6(O_2CCH_2C_6F_5)_8]$

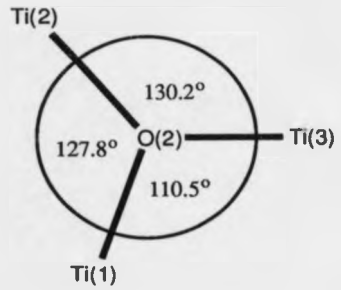
Table 5.2 Selected bond lengths for $[Ti_6O_4Cl_2(OEt)_6(O_2CCH_2C_6F_5)_8]$ (Å).

Ti(1)-Ti(3)	3.092(2)	Ti(1)-O(1)	1.728(5)
Ti(1)-O(2)	1.896(5)	Ti(1)-O(3)	2.104(5)
Ti(1)-O(12)	2.042(6)	Ti(1)-O(21)	2.004(7)
Ti(1)-O(42)	2.003(7)	Ti(1)-Ti(2a)	3.374(2)
Ti(2)-O(2)	1.896(5)	Ti(2)-O(4)	1.714(7)
Ti(2)-O(32)	2.043(6)	Ti(2)-Ti(1a)	3.374(2)
Ti(2)-O(1a)	1.901(5)	Ti(2)-O(11a)	2.062(6)
Ti(2)-O(22a)	2.107(7)	Ti(3)-Cl(1)	2.284(4)
Ti(3)-O(2)	2.093(5)	Ti(3)-O(3)	1.885(5)
Ti(3)-O(5)	1.719(6)	Ti(3)-O(31)	2.035(6)
Ti(3)-O(41)	2.104(7)	O(1)-Ti(2a)	1.901(5)
O(3)-C(301)	1.451(11)	O(4)-C(401)	1.373(20)
O(5)-C(501)	1.361(21)	O(11)-C(11)	1.233(10)
O(11)-Ti(2a)	2.062(6)	O(12)-C(11)	1.264(11)
O(21)-C(21)	1.249(12)	O(22)-C(21)	1.239(11)
O(22)-Ti(2a)	2.107(7)	O(31)-C(31)	1.231(11)
O(32)-C(31)	1.259(11)	O(41)-C(41)	1.231(12)
O(42)-C(41)	1.267(11)		

Table 5.3 Selected bond angles for $[Ti_6O_4Cl_2(OEt)_6(O_2CCH_2C_6F_5)_8]$ (°)

O(1)-Ti(1)-O(2)	107.8(2)	O(1)-Ti(1)-O(3)	175.3(2)
O(2)-Ti(1)-O(3)	76.9(2)	O(1)-Ti(1)-O(12)	92.0(2)
O(2)-Ti(1)-O(12)	160.2(2)	O(3)-Ti(1)-O(12)	83.3(2)
O(1)-Ti(1)-O(21)	93.5(3)	O(2)-Ti(1)-O(21)	91.3(2)
O(3)-Ti(1)-O(21)	86.1(2)	O(12)-Ti(1)-O(21)	86.9(3)
O(1)-Ti(1)-O(42)	94.5(3)	O(2)-Ti(1)-O(42)	91.6(2)
O(3)-Ti(1)-O(42)	85.4(2)	O(12)-Ti(1)-O(42)	87.3(3)
O(21)-Ti(1)-O(42)	170.3(2)	O(2)-Ti(2)-O(4)	101.5(3)
O(2)-Ti(2)-O(32)	91.1(2)	O(4)-Ti(2)-O(32)	95.8(3)
O(2)-Ti(2)-O(1a)	96.3(2)	O(4)-Ti(2)-O(1a)	97.1(3)
O(32)-Ti(2)-O(1a)	163.6(3)	O(2)-Ti(2)-O(11a)	167.7(3)
O(4)-Ti(2)-O(11a)	89.5(3)	O(32)-Ti(2)-O(11a)	82.2(2)
O(1a)-Ti(2)-O(11a)	87.7(2)	O(2)-Ti(2)-O(22a)	86.4(2)
O(4)-Ti(2)-O(22a)	171.5(3)	O(32)-Ti(2)-O(22a)	80.7(3)
O(1a)-Ti(2)-O(22a)	85.1(2)	O(11a)-Ti(2)-O(22a)	82.4(3)
Cl(1)-Ti(3)-O(2)	93.7(2)	Cl(1)-Ti(3)-O(3)	98.6(2)
O(2)-Ti(3)-O(3)	77.4(2)	Cl(1)-Ti(3)-O(5)	94.9(3)
O(2)-Ti(3)-O(5)	171.2(3)	O(3)-Ti(3)-O(5)	99.2(3)
Cl(1)-Ti(3)-O(31)	93.6(2)	O(2)-Ti(3)-O(31)	87.9(2)
O(3)-Ti(3)-O(31)	161.4(3)	O(5)-Ti(3)-O(31)	93.6(3)
Cl(1)-Ti(3)-O(41)	174.2(2)	O(2)-Ti(3)-O(41)	83.8(2)
O(3)-Ti(3)-O(41)	86.1(3)	O(5)-Ti(3)-O(41)	87.8(3)
O(31)-Ti(3)-O(41)	81.1(3)	Ti(1)-O(1)-Ti(2a)	136.7(3)
Ti(1)-O(2)-Ti(2)	127.8(2)	Ti(1)-O(2)-Ti(3)	101.5(2)
Ti(2)-O(2)-Ti(3)	130.2(3)	Ti(1)-O(3)-Ti(3)	101.5(2)
Ti(1)-O(3)-C(301)	130.7(5)	Ti(3)-O(3)-C(301)	127.3(5)
Ti(2)-O(4)-C(401)	160.0(7)	Ti(3)-O(5)-C(501)	163.9(12)
Ti(1)-O(12)-C(11)	129.4(5)	C(11)-O(11)-Ti(2a)	135.2(6)
Ti(1)-O(21)-C(21)	130.1(7)	O(11)-C(11)-O(12)	126.9(8)
O(21)-C(21)-O(22)	127.6(11)	C(21)-O(22)-Ti(2a)	134.2(7)
Ti(2)-O(32)-C(31)	132.8(6)	O(21)-C(21)-O(22)	115.9(8)
Ti(3)-O(41)-C(41)	128.9(6)	Ti(3)-O(31)-C(31)	137.5(6)
O(41)-C(41)-O(42)	126.9(10)	O(31)-C(31)-O(32)	126.9(9)
Ti(1)-O(42)-C(41)	127.4(7)		

The titanium μ_3-oxygen framework is shown below.



Ti(1)--O(2)	1.896Å
Ti(2)--O(2)	1.896Å
Ti(3)--O(2)	2.093Å

The difference in the Ti-O-Ti angles around the μ_3-O atom is most likely due to the constraints of the ligands bridging the titanium atoms. The summation of the angles around the μ_3-oxygen, O(2), yields a value of 359.5° and therefore Ti(1)-Ti(2)-Ti(3) are almost perfectly planar.

The μ_2-oxo bridge has Ti-O bond lengths of 1.728 and 1.901Å, again due to the presence of the bridging ethoxide group *trans* to the longer bond. The Ti(1)-O(1)-Ti(2a) angle of 136.7° is very similar to those found in compounds having the $[Ti_2(\mu_2\text{-}O)(\mu_2\text{-}O_2CR)_2]^{4+}$ unit such as $[\{TiCl_2(O_2CR)(RCO_2H)\}_2O]$ R=Et (137.3°), R=CMe_3 (138.3°) and $[\{TiCl_2(O_2CCH_2OC_6F_5)THF\}_2O]$ of 138.8° which are also reported in this thesis.

The titanium-oxygen bond lengths of the carboxylate ligands vary from 2.003-2.107Å. The O-C-O angles are more consistent with all being 126.9° except for O(22)-C(21)-O(21) which is slightly larger at 127.6°. Each O-C-O angle has increased from the ideal 120° and shows here that as well as the bridging oxygen atom being a flexible unit, the carboxylate ligand may also adjust to accommodate a larger Ti---Ti distance. The O-C-O angles of bridging carboxylate ligands in the unit $[Ti_2(\mu_2\text{-}O)(\mu_2\text{-}O_2CR)_2]^{4+}$ as discussed in Chapters 2 and 3 are somewhat smaller than this at 122-123°. In the latter case, the compounds were dinuclear species, but here the hexanuclear framework offers more constraints.

The large pentafluorophenylacetate ligands are orientated to eliminate close contacts and the effect of bulky carboxylate ligands does not appear to produce new oxo titanium species different to that of the acetate derivatives $[Ti_6O_4(O^nBu)_8(O_2CMe)_8]$[263] and $[Ti_6O_4(OEt)_8(O_2CMe)_8]$.[264]

The terminal Ti-Cl bond lengths on average is 2.284Å which is typical for titanium(IV) chloro linkages.

5.4. Further Room Temperature Reactions of $TiCl_4$ with Pentafluorophenylacetic and Pentafluorobenzoic Acids.

In the previous section it was observed that the reaction of $TiCl_4$ with pentafluorophenylacetic acid in the presence of ethanol resulted in the formation of the compound $[Ti_6O_4Cl_2(OEt)_6(O_2CCH_2C_6F_5)_8]$ which was isolated and subsequently structurally characterised.

The reaction was repeated, this time in carbon tetrachloride in the absence of ethanol with both 1:1 and 1:2 mole ratios of $TiCl_4$ to $C_6F_5CH_2CO_2H$. It was discovered that by utilising either of the reactant ratios, the same product was formed. The product contained titanium and pentafluorophenylacetate ligands in a ratio of 1:2. An analogous reaction was carried out in toluene using pentafluorobenzoic acid, and again it was discovered that the product was bis-substituted, and was formed independent of the reaction ratio. It is interesting that these room temperature reactions are in contrast to those of the alkyl acids $EtCO_2H$ and Me_3CCO_2H which have been reported in Chapter 2 where $[Ti_2Cl_7(O_2CR)(RCO_2H)]$ is formed at a 1:1 ratio of reactants, and $[\{TiCl_2(O_2CR)(RCO_2H)\}_2O]$ is produced at ratios of 1:2 and 1:2.5.

A related feature in the reactions of stronger acids has been observed previously by Kapoor and co-workers in the reaction of $TiCl_4$ with RCO_2H where R=CCl_3, $CHCl_2$ and CH_2Cl at -10°C, even when $TiCl_4$ is used in excess.[174] The products were formulated as $[TiCl_2(O_2CR)_2]$ but from the results obtained for this thesis it seems more likely that the products are of the formulation $[\{TiCl_2(O_2CR)(RCO_2H)\}_2O]$.

It is therefore not too surprising that $C_6F_5CO_2H$ and $C_6F_5CH_2CO_2H$ with $TiCl_4$ form a bis-substituted species at reactant ratios of 1:1. These acids are stronger in comparison to the alkyl acids which have been discussed in earlier chapters; $C_6F_5CO_2H$ has a pK_a of 1.73 while Me_3CCO_2H has a pK_a of 5.03.

From elemental analysis, the products of the reactions of pentafluorobenzoic and pentafluorophenylacetic acids may be formulated as $[\{TiCl_2(O_2CR)(RCO_2H)\}_2O]$ ($R=C_6F_5$, $CH_2C_6F_5$).

Preparation of $[\{TiCl_2(O_2CR)(RCO_2H)\}_2O]$ ($R=C_6F_5$, $CH_2C_6F_5$)

When $TiCl_4$ (1 mol) is added dropwise to a solution of RCO_2H ($R=C_6F_5$, $CH_2C_6F_5$) (2.5 mol) in toluene ($R=C_6F_5$) or carbon tetrachloride ($R=CH_2C_6F_5$) at room temperature, a yellow-orange solution is produced from which the title compounds may be isolated by the addition of petroleum ether. High yields of 80-85% are observed according to the equation below.

$$2TiCl_4 + 5RCO_2H \longrightarrow [\{TiCl_2(O_2CR)(RCO_2H)\}_2O] + RCOCl + 3HCl$$
$$(R=C_6F_5\ ,\ CH_2C_6F_5)$$

Again, the formulation of these particular binuclear oxo species is believed to proceed *via* the formation of acid chloride, which was found in the reaction liquors, from the reaction of $TiCl_4$ with the carboxylic acid. Elemental analysis agrees with the products being $[\{TiCl_2(O_2CC_6F_5)(C_6F_5CO_2H)\}_2O]$ and $[\{TiCl_2(O_2CCH_2C_6F_5)(C_6F_5CH_2CO_2H)\}_2O]$. These formulations are further supported by the IR and ^1H NMR spectra which will now be discussed.

IR Spectra of the species $[\{TiCl_2(O_2CR)(RCO_2H)\}_2O]$ ($R=C_6F_5$, $CH_2C_6F_5$)

Looking back to the IR data of the alkyl compounds $[\{TiCl_2(O_2CR)(RCO_2H)\}_2O]$ ($R=Me$, Et, CMe_3) which were discussed in Chapter 2, it is apparent that the broad hydroxyl stretching vibration centred at around $3200cm^{-1}$ is not observed in the title compounds. It

may be possible that a higher degree of association occurs between the molecules of $[\{TiCl_2(O_2CR)(RCO_2H)\}_2O]$ ($R=C_6F_5$, $CH_2C_6F_5$) than in the alkyl analogues. It is interesting to note also that the hydroxyl stretching band is not observed in the IR spectrum of the respective free carboxylic acids. Both intermolecular and intramolecular hydrogen bonding may occur, thus broadening [υ(OH)] so much that it may not be apparent in the IR spectra.

The $\upsilon(C=O)_{coord.acid}$ band may be assigned at 1613 ($R=C_6F_5$) and 1632cm^{-1} ($R=CH_2C_6F_5$) indicating that on co-ordination to the metal, the carbonyl stretching band has moved to lower wavenumbers by 104 ($R=C_6F_5$) and 82cm^{-1} ($R=CH_2C_6F_5$). This is in comparison to the shift observed on co-ordination of the alkyl acids to the titanium where values of 59 (R=Me), 68 (R=Et) and 54cm^{-1} ($R=CMe_3$) were recorded. The slight increase in this shift for the pentafluoro-aromatic acids would be consistent with the acid ligands being more strongly co-ordinated to the metal centre.

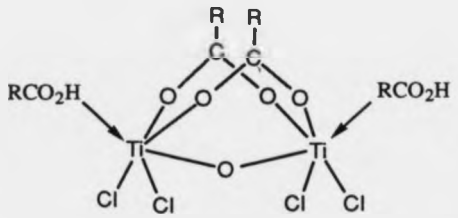
Only one set of asymmetric and symmetric carboxylate stretching bands are apparent in the IR spectrum of $[\{TiCl_2(O_2CR)(RCO_2H)\}_2O]$ ($R=C_6F_5$, $CH_2C_6F_5$). Thus $\upsilon(COO)_{asym}$ may be assigned to bands at 1543 ($R=C_6F_5$) and 1545cm^{-1} ($R=CH_2C_6F_5$) with bands at 1390 ($R=C_6F_5$) and 1385cm^{-1} ($R=CH_2C_6F_5$) being attributed to $\upsilon(COO)_{sym}$. The values of Δ are 153 ($R=C_6F_5$) and 160cm^{-1} ($R=CH_2C_6F_5$) which would support the proposal that in both compounds the carboxylate ligands are in a symmetrical bridging co-ordination mode.

The υ(Ti-O-Ti) vibration may be assigned to bands at 752 ($R=C_6F_5$) and 787cm^{-1} ($R=CH_2C_6F_5$) which are of weaker intensity and less broad than the corresponding bands in the analogous alkyl species.

Terminal Ti-Cl bands are present in the spectrum at 426, 398 and 362cm^{-1} ($R=C_6F_5$) and 420, 384 and 362cm^{-1} ($R=CH_2C_6F_5$). No absorption bands corresponding to υ(Ti-Cl) bridging vibrations are apparent.

^{1}H NMR Spectrum of [{$TiCl_2(O_2CCH_2C_6F_5)(C_6F_5CH_2CO_2H)$}$_2$O]

The ^{1}H NMR spectrum ($CDCl_3$) of the title compound is complicated by the fact that the signal patterns cannot, at this stage, be fitted to the proposed formulation. For the alkyl species, which have been discussed in Chapter 2, the following structure was observed in X-ray studies.



(R=Et, CMe_3)

Both the methyl and methylene signals of the alkyl groups in these latter derivatives were represented as multiplets in their ^{1}H NMR spectra.

Resonances for the compound [{$TiCl_2(O_2CCH_2C_6F_5)(C_6F_5CH_2CO_2H)$}$_2$O] appear at δ3.98 (2H), 3.97 (2H), 3.93 (10H) and 3.80 (2H). It is difficult to formulate a structure on the basis of these results and it may be that in solution there is more than one species present. Perhaps solution IR analysis could yield some information concerning the nature of any different species which may be present in solution. However, the hydroxyl proton of the co-ordinated acid molecules is present at δ9.02 as a very broad signal which adds to the validity of the proposed formulation of [{$TiCl_2(O_2CH_2C_6F_5)(C_6F_5CH_2CO_2H)$}$_2$O].

The methylene signals are all closely positioned within the range δ3.98-3.80 which leads to the suggestion that the carboxylate groups have similar bonding modes, but differ in their orientation within the molecule(s).

5.4.1. Further Investigations of $TiCl_4$ with Pentafluorophenylacetic Acid

For reasons which will become apparent in the next short section, the pentafluorophenylacetate derivative which has been discussed here will now be referred to as [{$TiCl_2(O_2CCH_2C_6F_5)(C_6F_5CH_2CO_2H)$}$_2$O] Form A.

Preparation of $[\{TiCl_2(O_2CCH_2C_6F_5)(C_6F_5CH_2CO_2H)\}_2O]$ Form B

In addition to Form A, a further species has been isolated from a room temperature reaction carried out using similar conditions. From elemental analysis it is apparent that this new compound has a similar formulation with a Ti : carboxylate ratio of 1:2. Thus on addition of $TiCl_4$ (1 mol) to a solution of pentafluorophenylacetic acid (2.5 mol) in chloroform instead of carbon tetrachloride, at room temperature, a yellow solution results which on carefully layering with light petroleum and standing for 2 weeks gives a cream 'furry-looking' precipitate. This compound is also formulated as $[\{TiCl_2(O_2CCH_2C_6F_5)(C_6F_5CH_2CO_2H)\}_2O]$ on the basis of elemental, IR and ^1H NMR analyses which will now be referred to as $[\{TiCl_2(O_2CCH_2C_6F_5)(C_6F_5CH_2CO_2H)\}_2O]$ Form B. This latter compound is formed by the now familiar route

$$2TiCl_4 + 5C_6F_5CH_2CO_2H \xrightarrow{CHCl_3 / r.t.} [\{TiCl_2(O_2CCH_2C_6F_5)(C_6F_5CH_2CO_2H)\}_2O] + C_6F_5CH_2COCl + 3HCl$$

Acid chloride was clearly present in the reaction liquors and was identified from IR spectral studies. The product was characterised by IR and ^1H NMR spectroscopy which will now be discussed.

IR Spectrum of $[\{TiCl_2(O_2CCH_2C_6F_5)(C_6F_5CH_2CO_2H)\}_2O]$ Form B

The IR spectra of $[\{TiCl_2(O_2CCH_2C_6F_5)(C_6F_5CH_2CO_2H)\}_2O]$ Forms A and B, in the region 1800-1200cm^{-1} are shown in Figure 5.3 overleaf, for comparison.

As is evident from the spectrum of Form B, a very high carboxylate stretching band is observed at 1687cm^{-1} which would tend to be indicative of monodentate carboxylate ligation as discussed in Chapter 1. Alternatively, it could possibly be the carbonyl stretching signal of the co-ordinated acid. However, in view of the overall spectrum the band is best assigned to $\upsilon(COO)_{asym}$ of a monodentate pentafluorophenylacetate ligand. Pertinent IR data of the title compound is given in Table 5.4 along with Form A.

Figure 5.3 The IR spectra of [{$TiCl_2(O_2CCH_2C_6F_5)(C_6F_5CH_2CO_2H)_2O$] Forms A and B in the region 1800-1200cm^{-1}.

Table 5.4 Pertinent IR data (cm^{-1}) for the compounds $[\{TiCl_2(O_2CCH_2C_6F_5)(C_6F_5CH_2CO_2H)\}_2O]$ Forms A and B

Form	υ(C=O) coord.acid	$\upsilon(COO)_{asym}$	$\upsilon(COO)_{sym}$	Δ	υ(Ti-O-Ti)	υ(Ti-Cl)
A	1632	1545	1385	160	787	420, 384, 362
B	1606	1687 1548	1395 1390	292 158	740	456, 385, 280

As with $[\{TiCl_2(O_2CC_6F_5)(C_6F_5CO_2H)\}_2O]$ and Form A, no broad hydroxyl stretching band of the co-ordinated carboxylic acid ligand is observed at $3200cm^{-1}$, although the presence of the co-ordinated acid is indicated in the ^1H NMR spectrum.

As may be seen by reference to Table 5.4, for Form B the carboxylate asymmetric and symmetric stretching bands which have been assigned give values of Δ of 292 and $158cm^{-1}$, which are indicative of monodentate and bidentate carboxylate co-ordination respectively. $[\{TiCl_2(O_2CCH_2C_6F_5)(C_6F_5CH_2CO_2H)\}_2O]$ Form B is the only example in the compounds which have been prepared for this thesis where monodentate ligation apparently occurs. This could be a consequence of the weaker Lewis basicity of the pentafluorophenylacetate ion in comparison to those of the alkyl acids. However, conclusive evidence for the nature of the carboxylate co-ordination may only be gained from an X-ray structure determination. Unfortunately, the compound $[\{TiCl_2(O_2CCH_2C_6F_5)(C_6F_5CH_2CO_2H)\}_2O]$ Form B appears to crystallise as a 'furry' mass rather than as single crystals. It may be possible that a similar compound exists for pentafluorobenzoic acid with $TiCl_4$.

The presence of a μ_2-O bridge in a [Ti-O-Ti] fragment is indicated by a band at $740cm^{-1}$. Strong bands at 456 and $385cm^{-1}$ are assigned to υ(Ti-Cl) terminal vibrations while the broad strong band centred at $280cm^{-1}$ is assigned to a bridging υ(Ti-Cl) mode.

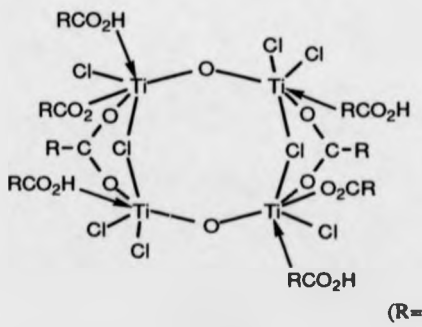
^{1}H NMR Spectrum of [{$TiCl_2(O_2CCH_2C_6F_5)(C_6F_5CH_2CO_2H)$}$_2$O] Form B

It is reasonable to anticipate that the presence of two different types of carboxylate ligation could be identified from the ^{1}H NMR spectrum, but the title compound shows only a very broad band centred at δ9.51 and four bands identically positioned to those of Form A at δ3.98 (2H), 3.97 (2H), 3.93 (10) and 3.80 (2H). This indicates that in solution, Form A and Form B are identical. The presence of the hydroxyl proton signal at δ9.51 confirms the presence of co-ordinated pentafluorophenylacetic acid ligands. Again as discussed for Form A, no structural evidence has so far been able to be gained from the ^{1}H NMR spectrum.

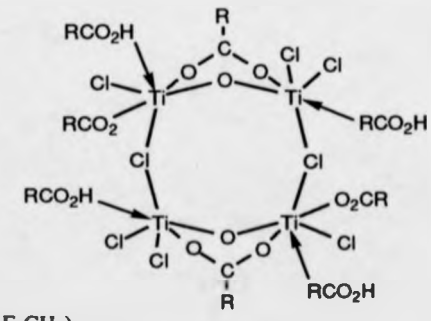
As mentioned previously, it would be very interesting in light of these results to study the solution IR spectra of both forms to check that they were the same. In comparison, we have seen that the nujol mull spectra of the two compounds are very different; Form A showing bidentate ligation and Form B exhibiting both monodentate and bidentate co-ordination.

5.4.2. Possible Structure for [{$TiCl_2(O_2CCH_2C_6F_5)(C_6F_5CH_2CO_2H)$}$_2$O] Form B

In light of the IR spectral data it is proposed that the title compound contains both unidentate and bidentate carboxylate ligands, co-ordinated pentafluorophenylacetic acid and also both terminal and chlorine ligands. Two possible structures **(5.3)** and **(5.4)** may therefore be postulated that fit the requirements.



(5.3)



(R=$C_6F_5CH_2$)

(5.4)

CHAPTER SIX

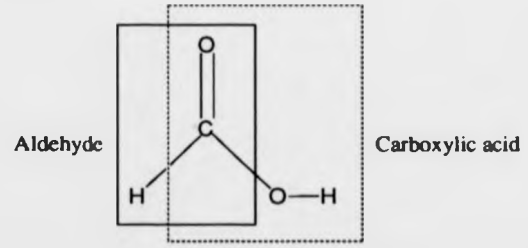
HIGH TEMPERATURE REACTIONS OF $TiCl_4$ WITH THE ACIDS RCO_2H ($R=C_6F_5$, $CH_2C_6F_5$, $CH_2OC_6F_5$)

6. INTRODUCTION

Previous chapters have introduced some of the titanium carboxylate species which have been prepared both in this laboratory and other research groups. In this next short section, further carboxylate species will be discussed which will conclude the survey of these compounds.

6.1. Further Titanium Carboxylate Species

The reaction of $TiCl_4$ with formic acid has been investigated independently by both Kapoor and co-workers and Nirsha *et al* . The addition of $TiCl_4$ (1 mol) to formic acid (2 mol) in dichloromethane at -78°C with subsequent warming to -10°C produces a yellow resinous material which Kapoor *et al* analysed as $[TiCl_2(O_2CH)_2]$.[178] It may be possible that the formic acid adduct $[\{TiCl_2(O_2CH)(HCO_2H)\}_2O]$ was prepared, as analytical values for both the bis-carboxylate and the oxo bridged species are very similar. However, the IR spectrum of the titanium formate showed absorption bands assigned to $\upsilon(COO)_{asym}$ at 1540 and $\upsilon(COO)_{sym}$ at 1355cm^{-1}. No band at 1650cm^{-1} was reported which may be assigned to $\upsilon(C{=}O)$ of the co-ordinating acid as in the species $[\{TiCl_2(O_2CR)(RCO_2H)\}_2O]$ (R=Me, Et, CMe_3) which were reported in Chapter 2. Formic acid, HCO_2H, is different to the acids higher in the homologous series due to it possessing both a carboxylic acid functionality and an aldehyde moiety **(7.1)**. This factor could effect the reaction of the acid with $TiCl_4$ in that products of different stoichiometry than those obtained with acetic, propanoic and trimethylacetic acids may be produced.



(7.1)

Refluxing the contents of the above reaction (40°C) gave a yellow solid after 30 minutes which analysed as $[TiCl_2(O_2CH)(OH)]$. Both $[TiCl_2(O_2CH)_2]$ and $[TiCl_2(O_2CH)(OH)]$ are highly hygroscopic. This latter compound has an unusual formulation which has not been encountered in studies carried out for this thesis, and may possibly be the result of a misformulation. At higher temperatures, refluxing the acid (2 mol) with $TiCl_4$ (1 mol) for 24 hours produced a white precipitate which was formulated as $[Ti(OH)_2(O_2CH)_2]$. The IR spectrum of this air stable compound showed absorption bands at 1560 and 1365cm^{-1} which were assigned to $\upsilon(COO)_{asym}$ and $\upsilon(COO)_{sym}$ respectively, however no IR evidence for the Ti-OH moieties in the compounds $[TiCl_2(O_2CH)(OH)]$ and $[Ti(OH)_2(O_2CH)_2]$ were reported.

In contrast, Nirsha and co-workers investigated reactions involving $TiCl_4$ and formic acid in a 1:4 ratio at temperatures of 100-120°C and reported the reaction product as $[Ti_2OCl(O_2CH)_3(OH)_2]$, yet another formulation which is unsupported by structural evidence.[265] Little information was reported, but the authors noted the presence of absorption bands in the IR spectrum which could be assigned to υ(Ti-O-Ti) at 780cm^{-1} and υ(Ti-O) at 440cm^{-1}.

With a view to preparing $[Ti(O_2CMe)_4]$, the reaction between $TiCl_4$ and acetic anhydride has been investigated by Mehrotra and co-workers. An initial exothermic reaction appeared to produce the compound $[TiCl_2(O_2CMe)_2]$ which we now know from studies for this thesis is the oxo bridged binuclear species $[\{TiCl_2(O_2CMe)(MeCO_2H)\}_2O]$. Refluxing this reaction mixture gave a thick green precipitate which corresponded on analysis to a tri-acetate compound of the formulation $[Ti_2O(O_2CMe)_6]$.[266]

A similar reaction scheme is reported to occur in the reaction of acetic acid with $TiCl_4$.[267] The following reaction scheme was proposed.

$$TiCl_4 + MeCO_2H \xrightarrow{fast} [TiCl_3(O_2CMe)] + HCl$$

$$[TiCl_3(O_2CMe)] + MeCO_2H \xrightarrow{fast} [TiCl_2(O_2CMe)_2] + HCl$$

$$[TiCl_2(O_2CMe)_2] + MeCO_2H \xrightarrow{slow} [TiCl(O_2CMe)_3] + HCl$$

$$[TiCl(O_2CMe)_3] \xrightarrow{decomposition} [TiO(O_2CMe)_2] + MeCOCl$$

An additional reaction may also occur, *viz:*

$$[TiCl(O_2CMe)_3] + [TiCl_2(O_2CMe)_2] \longrightarrow [\{TiCl(O_2CMe)_2\}_2O] + MeCOCl$$

If a large amount of acid is present this could be followed by

$$[\{TiCl(O_2CMe)_2\}_2O] + 2MeCO_2H \longrightarrow [\{Ti(O_2CMe)_3\}_2O] + 2HCl$$

Unfortunately, no spectral data was given for these derivatives, and the final product appeared to be characterised by elemental analysis only.

Species of the type $[TiO(O_2CR)_2]$ have been reported by a number of research groups by different preparative routes.

The controlled hydrolysis of a mixed alkoxide / carboxylate titanium(IV) complex has been found to follow the route of the equation below.[268]

$$[Ti(O_2CR)_2(OCHMe_2)_2] \xrightarrow[reflux]{H_2O} [TiO(O_2CR)_2] + 2Me_2CHOH$$

$(R=C_7\text{-}C_{21}$ alkyl)

The IR spectra of these species are reported as showing two types of carboxylates with an absorption band at 1730cm^{-1} assigned to υ(C=O) of a unidentate carboxylate and bands at 1560 and 1450cm^{-1} assigned to $\upsilon(COO)_{asym}$ and $\upsilon(COO)_{sym}$ respectively of a bidentate carboxylate. Compounds prepared for this thesis of the type $[TiO(O_2CR)_2]$, which will shortly be discussed, have not been found to exhibit two sets of carboxylate stretching bands in their IR spectra, and no carboxylate bands higher than 1570cm^{-1} have been observed. It may therefore be possible that the long chain of the fatty acids result in a different structure. What also seems likely is that the band at 1730cm^{-1} for the fatty acid carboxylates is due to the υ(C=O) of free acid which may not have been completely removed

$$TiCl_4 + MeCO_2H \xrightarrow{fast} [TiCl_3(O_2CMe)] + HCl$$

$$[TiCl_3(O_2CMe)] + MeCO_2H \xrightarrow{fast} [TiCl_2(O_2CMe)_2] + HCl$$

$$[TiCl_2(O_2CMe)_2] + MeCO_2H \xrightarrow{slow} [TiCl(O_2CMe)_3] + HCl$$

$$[TiCl(O_2CMe)_3] \xrightarrow{decomposition} [TiO(O_2CMe)_2] + MeCOCl$$

An additional reaction may also occur, *viz:*

$$[TiCl(O_2CMe)_3] + [TiCl_2(O_2CMe)_2] \longrightarrow [\{TiCl(O_2CMe)_2\}_2O] + MeCOCl$$

If a large amount of acid is present this could be followed by

$$[\{TiCl(O_2CMe)_2\}_2O] + 2MeCO_2H \longrightarrow [\{Ti(O_2CMe)_3\}_2O] + 2HCl$$

Unfortunately, no spectral data was given for these derivatives, and the final product appeared to be characterised by elemental analysis only.

Species of the type $[TiO(O_2CR)_2]$ have been reported by a number of research groups by different preparative routes.

The controlled hydrolysis of a mixed alkoxide / carboxylate titanium(IV) complex has been found to follow the route of the equation below.[268]

$$[Ti(O_2CR)_2(OCHMe_2)_2] \xrightarrow[reflux]{H_2O} [TiO(O_2CR)_2] + 2Me_2CHOH$$

$(R=C_7\text{-}C_{21}$ alkyl)

The IR spectra of these species are reported as showing two types of carboxylates with an absorption band at 1730cm^{-1} assigned to υ(C=O) of a unidentate carboxylate and bands at 1560 and 1450cm^{-1} assigned to $\upsilon(COO)_{asym}$ and $\upsilon(COO)_{sym}$ respectively of a bidentate carboxylate. Compounds prepared for this thesis of the type $[TiO(O_2CR)_2]$, which will shortly be discussed, have not been found to exhibit two sets of carboxylate stretching bands in their IR spectra, and no carboxylate bands higher than 1570cm^{-1} have been observed. It may therefore be possible that the long chain of the fatty acids result in a different structure. What also seems likely is that the band at 1730cm^{-1} for the fatty acid carboxylates is due to the υ(C=O) of free acid which may not have been completely removed

from the solid product. The authors propose the presence of bridging rather than terminal oxygen ligands due to the presence of a broad band at 835cm^{-1} which was assigned υ(Ti-O-Ti).

Sartori and Weidenbruch reported the preparation of the titanium oxo carboxylates $[TiO(O_2CR)_2]$ (R=CF_3, C_2F_5, C_3F_7) by the addition of $TiCl_4$ or $TiBr_4$ to the carboxylic acid with heating to 60°C.[269] An oligomeric structure was postulated on the basis of υ(Ti-O-Ti) assigned at 780cm^{-1} in the IR spectrum. Using trifluoroacetic acid, the carboxylate adduct $[\{TiO(O_2CCF_3)_2\}_3.2CF_3CO_2H]$ crystallised from solution which on heating in high vacuum produces $[TiO(O_2CCF_3)_2]$.

The following reaction scheme in the preparation of the species $[TiO(O_2CR)_2]$ (R=CF_3, C_2F_5, C_3F_7) was proposed.

$$TiCl_4 + 4CF_3CO_2H \longrightarrow [TiO(O_2CCF_3)_2] + (CF_3CO)_2O + HCl$$
$$(CF_3CO)_2O + HCl \longrightarrow CF_3CO_2H + CF_3COCl$$

Kapoor's attempts to prepare titanium tetra-carboxylate species failed, even on using a large excess of carboxylic acid, and only compounds of the type $[TiO(O_2CR)_2]$ (R=Me, Et, ^{n}Pr, ^{n}Bu, ^{n}Pentyl) were isolated.[174] We have seen in previous chapters that new oxo carboxylate species of propanoic and trimethylacetic acids have been prepared at temperatures of greater than 60°C, but the compounds prepared for this thesis were formulated as $[Ti_3O_2Cl_3(O_2CR)_5]$ (R=Et, CMe_3) and $[\{TiCl(O_2CCMe_3)_2\}_2O]$. We have found no evidence for the existence of $[TiO(O_2CR)_2]$ where R=alkyl. The compounds reported by Kapoor exhibited a single asymmetric carboxylate band at 1570cm^{-1} which suggested that the carboxylates in the molecule were all symmetrically related. The authors note that a strong, broad band centred in the range 700-800cm^{-1} is observed in the IR spectra of the $[TiO(O_2CR)_2]$ species which they assigned to υ(Ti-O-Ti) and suggested that Ti-O-Ti-O chains were present.

6.2. High Temperature Reactions Utilising Pentafluorobenzoic and Pentafluorophenylacetic Acids

In addition to investigating the room temperature reactions of pentafluorobenzoic and pentafluorophenylacetic acid, high temperature reactions were carried out in an attempt to synthesise and characterise new titanium carboxylate species so that a more comprehensive overview of the reactions of $TiCl_4$ with these stronger carboxylic acids could be obtained. As a result of these high temperature experiments, air stable compounds were produced which analysed as $[TiO(O_2CR)_2]$ ($R=C_6F_5$, $CH_2C_6F_5$). X-ray diffraction study of the pentafluorobenzoate dervative revealed an unusual octameric structure containing only μ_2-carboxylate and μ_2-oxo ligands.

6.2.1. Preparation of the species $[TiO(O_2CR)_2]$ ($R=C_6F_5$, $CH_2C_6F_5$)

The addition of $TiCl_4$ (1 mol) to a solution of the carboxylic acid, RCO_2H ($R=C_6F_5$, $CH_2C_6F_5$) (3 mol) in toluene, produces an orange solution which on refluxing for 3-5 hours pales to a yellow-orange. For $R=C_6F_5$, the reaction solution is layered with light petroleum ether and left to stand for 1-2 weeks, within which time golden yellow crystalline cubes are deposited. The pentafluorophenylacetate species may be isolated by removal of the solvent until approximately $10cm^3$ of toluene remains and then adding a large amount ($\sim 100cm^3$) of petroleum ether. The resultant solution is then kept at -10°C for approximately 1 week to enable precipitation of the product. The pentafluorophenylacetate derivative appears to have much greater solubility than $[TiO(O_2CC_6F_5)_2]$, most probably due to the presence of the methylene group in the molecule. This solubility is most likely a major factor in the low yield of the product which is isolated (50%) in comparison to that for the pentafluorobenzoate derivative (80%).

Both $[TiO(O_2CR)_2]$ ($R=C_6F_5$, $CH_2C_6F_5$) were characterised by elemental analysis and IR spectroscopy and $[TiO(O_2CCH_2C_6F_5)_2]$ was additionally characterised by ^1H NMR spectroscopy. X-ray diffraction studies were carried out on suitable crystals of

$[TiO(O_2CC_6F_5)_2]$ which indicated that the compound was a cyclic octameric carboxylate which contained no terminal ligands.

The spectral properties of these compounds will now be discussed.

The IR Properties of the compounds $[TiO(O_2CR)_2]$ ($R=C_6F_5$, $CH_2C_6F_5$)

The IR spectra of the title compounds both show two bands in the region 1600-1350cm^{-1} which may be attributed to carboxylate stretching vibrations. Absorption bands positioned at 1576 ($R=C_6F_5$) and 1572cm^{-1} ($R=CH_2C_6F_5$) may be assigned to $\upsilon(COO)_{asym}$ and bands at 1400 ($R=C_6F_5$) and 1398cm^{-1} ($R=CH_2C_6F_5$) are labelled as $\upsilon(COO)_{sym}$. Thus, the values of Δ [$\upsilon(COO)_{asym}$-$\upsilon(COO)_{sym}$] are 176 ($R=C_6F_5$) and 174cm^{-1} ($R=CH_2C_6F_5$). These Δ values are higher than those found for the alkyl oxo species reported in this thesis. However, on comparison with that of $[Na(O_2CMe)]$ (164cm^{-1}),[121] the sodium salt of pentafluorobenzoate has $\upsilon(COO)_{asym}$ and $\upsilon(COO)_{sym}$ of 1610 and 1400cm^{-1} respectively, thus giving a Δ value of 210cm^{-1}.[270] The ionic carboxylate stretching bands of the pentafluorophenylacetate are very likely to be also in this region. In general, Δ appears to be greater for ionic species of stronger carboxylic acids. As a further comparison, the Δ values of $[Na(O_2CCF_3)]$[271] and $[K(O_2CCF_3)]$[272] are 223 and 241cm^{-1} respectively; also considerably higher than that of the acetate discussed above. In line with these figures, higher bridging values of Δ have been found for trifluoroacetate compounds relative to the acetate derivatives, such as $[Ag(O_2CCF_3)_2]$[273] (169cm^{-1}) and $[CpV(O_2CCF_3)_2]$[274] (245cm^{-1}). In addition to this information, $[Ti_6O_4Cl_2(OEt)_6(O_2CCH_2C_6F_5)_8]$ which has been discussed in the previous chapter, contains only bridging pentafluorophenylacetate groups and exhibits high Δ values of 166 and 171cm^{-1}. Therefore, it would appear that the Δ values of 176cm^{-1} for $[TiO(O_2CC_6F_5)_2]$ and 174cm^{-1} for $[TiO(O_2CCH_2C_6F_5)_2]$ appear to indicate that bridging carboxylate ligands are present in the molecules. Indeed, the crystal structure analysis of $[TiO(O_2CC_6F_5)_2]$ shows that all the pentafluorobenzoate ligands are symmetrically bridging, and it is therefore concluded that the pentafluorophenylacetate derivative has an analogous structure.

Compounds of the type $[TiO(O_2CR)_2]$ (R=CCl_3, $CHCl_2$, CH_2Cl, Me, Et, ^nPr, ^nBu, ^{n}Pentyl) have been prepared previously by Kapoor and co-workers, as discussed in the introduction to this chapter.[174] The products were characterised by elemental analysis and IR spectroscopy, the latter of which is displayed in Table 6.1.

Table 6.1 Reaction and IR spectral data (cm^{-1}) for compounds of the type $[TiO(O_2CR)_2]$.[174]

Acid	Molar ratio $TiCl_4$:Acid	Reaction conditions	Product	υ(COO) asym	υ(COO) sym	Δ
CCl_3CO_2H	1:4.5	Refl. in CCl_4	$[TiO(O_2CCCl_3)_2]$	1585	1380	205
$CHCl_2CO_2H$	1:4.5	Refl. in CCl_4	$[TiO(O_2CCHCl_2)_2]$	1570	1405	165
CH_2ClCO_2H	1:4.5	Refl. in CCl_4	$[TiO(O_2CCH_2Cl)_2]$	1565	1420	145
$MeCO_2H$	1:20	Refluxed	$[TiO(O_2CMe)_2]$	1565	1415	150
$EtCO_2H$	1:20	Refluxed	$[TiO(O_2CEt)_2]$	1570	1410	160
$^nPrCO_2H$	1:20	Refluxed	$[TiO(O_2C^nPr)_2]$	1570	1415	155
$^nBuCO_2H$	1:20	Refluxed	$[TiO(O_2C^nBu)_2]$	1580	1420	160
^{n}PentylCO$_2$H	1:20	Refluxed	$[TiO(O_2C^n$Pentyl$)_2]$	1570	1410	160

As can be seen from the spectral data in Table 6.1, the asymmetric and symmetric carboxylate stretching vibrations are very similarly positioned to those found for the pentafluorobenzoate and pentafluorophenylacetate derivatives. The differing reactant ratios used in the preparations possibly illustrates the ease with which the reaction occurs, thus the stronger chloro acids react more easily than the alkyl acids to produce $[TiO(O_2CR)_2]$ species.

Kapoor proposed that these compounds contained $(Ti\text{-}O\text{-}Ti\text{-}O)_n$ chains due to the presence of a strong broad band centred in the range 700-800cm^{-1} which was assigned to υ(Ti-O-Ti).

For $[TiO(O_2CR)_2]$ (R=C_6F_5, $CH_2C_6F_5$) bands at 769 (R=C_6F_5) and 782cm^{-1} (R=$CH_2C_6F_5$) are tentatively assigned to υ(Ti-O-Ti). This is in line with the values reported by Sartori and Weidenbruch in the preparation of $[TiO(O_2CR)_2]_n$ (R=CF_3, C_2F_5,

C_3F_7). Absorption bands at 780cm^{-1} in the IR spectrum of the three fluoro compounds were assigned to υ(Ti-O-Ti).[269]

$[TiO(O_2CC_6F_5)_2]$ and $[TiO(O_2CCH_2C_6F_5)_2]$ are not air sensitive, primarily due to the absence of Ti-Cl bonds as confirmed by the IR spectra which contain no apparent terminal or bridging Ti-Cl absorption bands in the 450-200cm^{-1} region.

The titanium-carboxylate bonds in $[TiO(O_2CR)_2]$ (R=C_6F_5, $CH_2C_6F_5$) do not appear to hydrolyse in air to produce titanium dioxide and the carboxylic acid.

$$[TiO(O_2CR)_2] + H_2O \not\longrightarrow TiO_2 + 2RCO_2H$$

^{1}H NMR Spectrum of the compound $[TiO(O_2CCH_2C_6F_5)_2]$

The ^{1}H NMR spectrum of the pentafluorophenylacetate derivative shows two singlets at δ3.81 and 3.40, as shown in Figure 6.1, overleaf. The singlets are in a 1: 1 ratio. This would appear to suggest that there are two sets of carboxylate ligands in very different environments, or possibly the presence of two different bonding modes for the pentafluorophenylacetate ligands. This latter suggestion is not evident from the IR spectrum of the compound and therefore it would seem likely that the two singlets are a consequence of the spatial arrangement of the ligands.

The X-ray structure of the pentafluorobenzoate derivative will be discussed in detail shortly, but for an explanation as to the formation of the two singlets it is best to view this structure parallel to the Ti-μ_2-O plane (Figure 6.4). As is evident from the structure, eight carboxylate ligands are approximately within the plane of the Ti-μ_2-O ring, and the other eight alternate below and above. The field of the bridging oxygen atom may possibly influence the two sets of carboxylate ligands differently, therefore causing two signals for the methylene protons to be observed in the ^{1}H NMR spectrum.

Alternatively, the two singlets may signify that, in solution, a different species exists having both monodentate and bridging ligands. However, for this to occur the co-ordination number would be reduced from six to five. More information is needed to assess what is

happening in solution to the pentafluorophenylacetate species. An IR spectrum of the solution would be useful since the presence of monodentate carboxylate ligands would be signified by $\upsilon(COO)_{asym}$ being much higher than that found in the solid state spectrum corresponding to the $\upsilon(C{=}O)$ moiety.

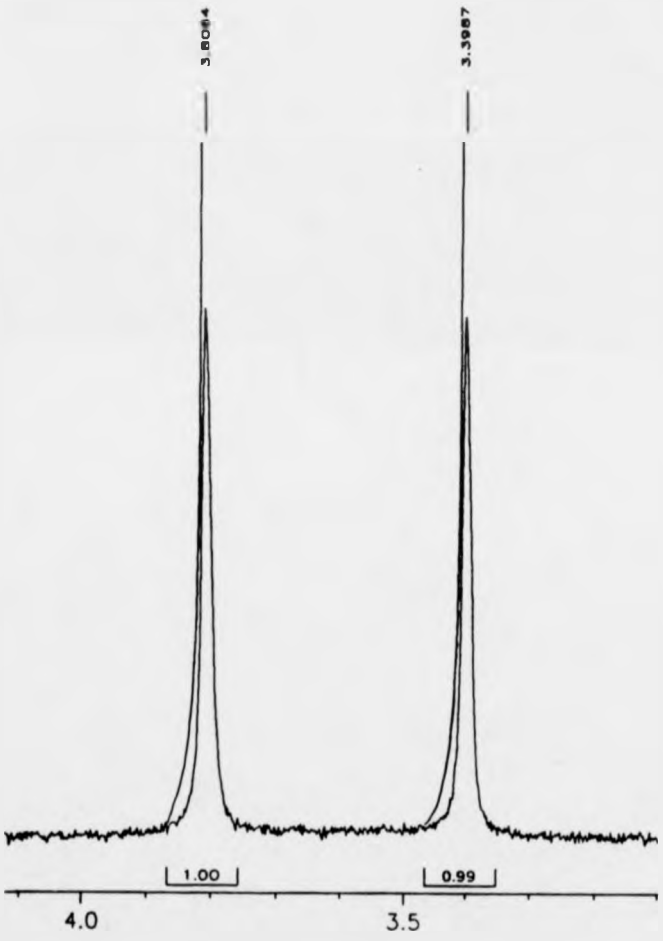


Figure 6.1 ^1H NMR spectrum of $[TiO(O_2CCH_2C_6F_5)_2]$

6.2.2. X-Ray Crystal Structure Determination of the compound $[\{TiO(O_2CC_6F_5)_2\}_8].nC_7H_8$ (n approx. 6)

Crystals suitable for X-ray diffraction were obtained from slow diffusion of a toluene / petroleum ether solution as yellow blocks.

The X-ray crystallographic study revealed the presence of a cyclic octameric structure comprising of $[Ti_2(\mu_2\text{-}O)(\mu_2\text{-}O_2CC_6F_5)_2]^{4+}$ repeating units. This is the first example of a metal carboxylate structure of this type.

The structure of $[\{TiO(O_2CC_6F_5)_2\}_8]$ is shown in Figures 6.2, 6.3 and 6.4, and selected bond lengths and bond angles are displayed in Tables 6.2 and 6.3 respectively.

As can be seen from reference to Figures 6.2-6.4, in the solid state $[TiO(O_2CC_6F_5)_2]$ exists as an octameric species. The titanium atoms are each in a distorted octahedral environment and form a nearly regular octagon with the average adjacent Ti---Ti distance being 3.323Å, thus eliminating the possibility of any metal-metal interaction.

Each adjacent pair of titanium atoms is bridged by a single oxide ion and two pentafluorobenzoate anions. The bridging oxygens are almost in the same plane as the titaniums, deviating slightly in an alternating manner. The greatest deviation from the best plane of the titanium atoms is 0.599Å. The bridging oxygens are inside the ring of the titanium atoms with an average $Ti\text{-}O_{oxo}\text{-}Ti$ bond angle of 135.4° which is similar to the μ-oxo angles in the binuclear carboxylate supported units of $[\{TiCl_2(O_2CR)(RCO_2H)\}_2O]$ (R=Et, 137.3°; R=CMe_3, 138.3°) and $[\{TiCl_2(O_2CCH_2OC_6F_5)THF\}_2O]$ (138.8°) which have been prepared and discussed earlier in Chapters 2 and 3. The average $Ti\text{-}O_{oxo}$ distance is 1.796Å which is also comparable with those found in the above three species of 1.794, 1.769 and 1.78Å respectively.

Comparison with the average $Ti\text{-}O_{carboxylate}$ bond length of 2.026Å indicates that some additional pπ-dπ bonding occurs in the μ_2-oxo bridge thus shortening the Ti-O-Ti bonds. The angles between the bridging oxygens at each titanium [O-Ti-O] are on average 100°, which shows an increase from the ideal 90°.

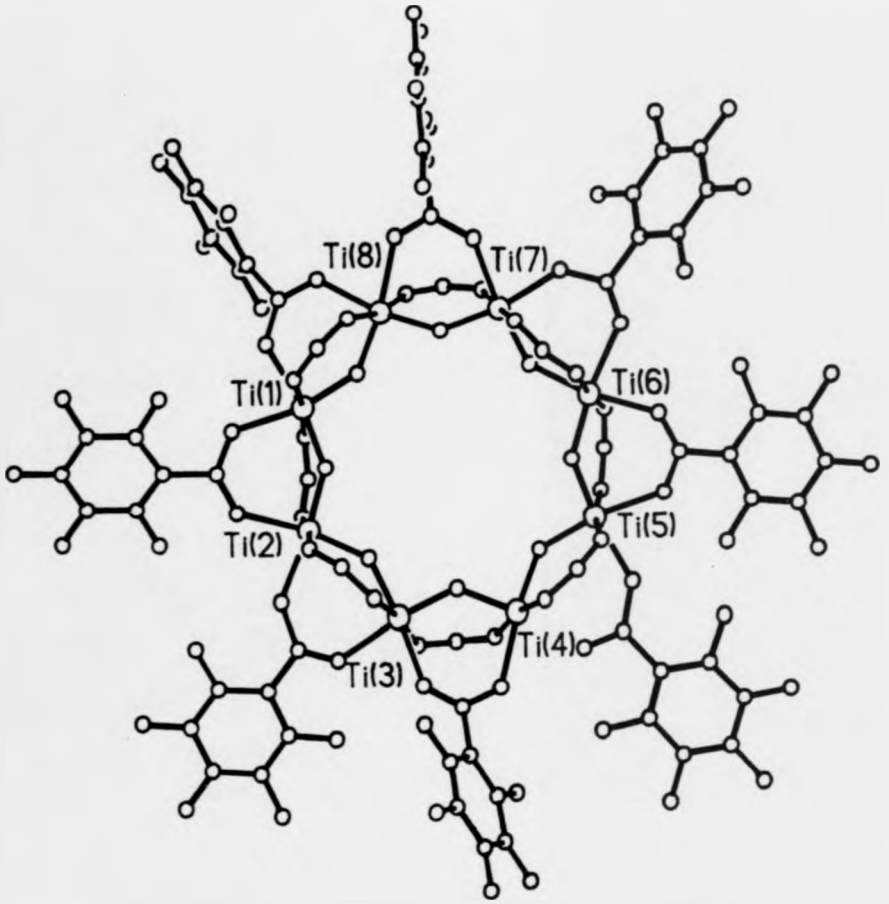


Figure 6.2 Partial structure of $[\{TiO(O_2CC_6F_5)_2\}_8]$ (removing all but the α-carbon atoms of the axial carboxylates).

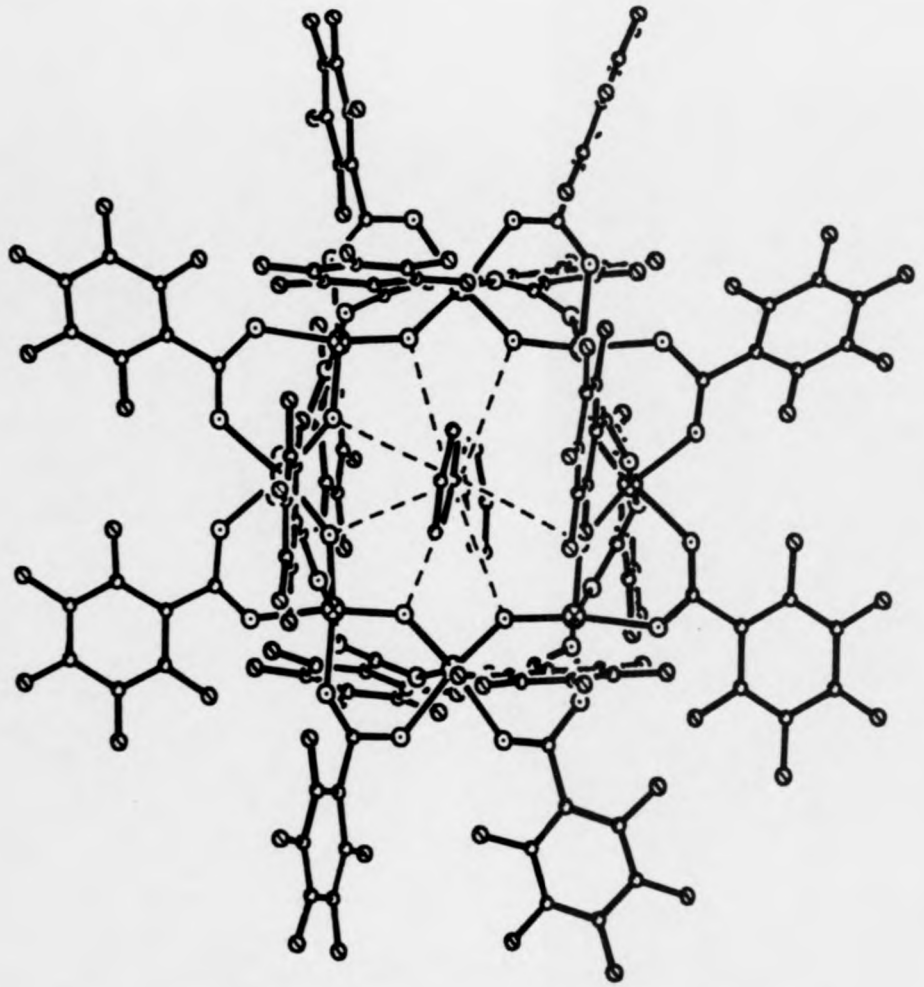


Figure 6.3 Full structure of $[\{TiO(O_2CC_6F_5)_2\}_8]$ viewed end-on to the ring showing the two encapsulated toluene molecules.

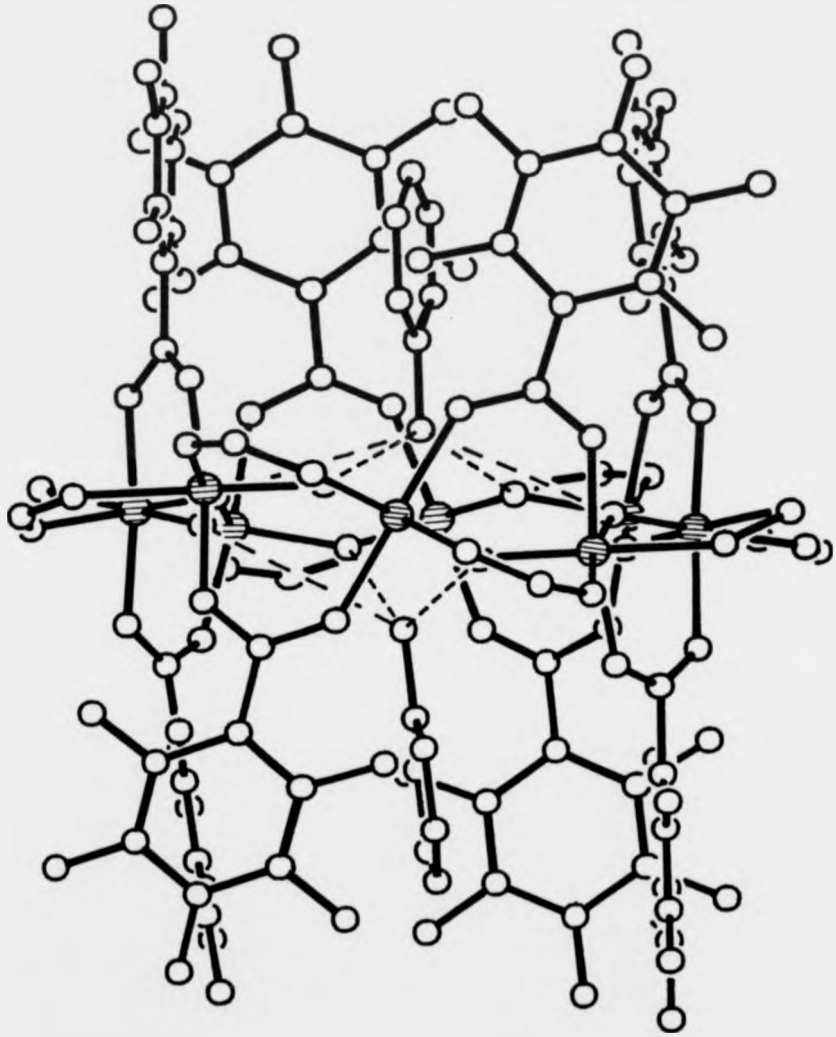


Figure 6.4 Partial structure of $[\{TiO(O_2CC_6F_5)_2\}_8]$ viewed parallel to the ring (removing all but the α-carbon atoms of the equatorial carboxylates).

Table 6.2 Selected bond lengths for $[\{TiO(O_2CC_6F_5)_2\}_8]$ (Å)

Ti(1)-O(12)	1.785(17)	Ti(1)-O(81)	1.759(22)
Ti(1)-O(121)	2.066(24)	Ti(1)-O(211)	2.003(23)
Ti(1)-O(181)	2.078(18)	Ti(1)-O(811)	2.012(25)
Ti(2)-O(12)	1.794(20)	Ti(2)-O(23)	1.782(24)
Ti(2)-O(122)	2.044(25)	Ti(2)-O(212)	1.970(21)
Ti(2)-O(231)	2.034(20)	Ti(2)-O(321)	1.936(21)
Ti(3)-O(23)	1.812(19)	Ti(3)-O(34)	1.796(25)
Ti(3)-O(232)	2.052(26)	Ti(3)-O(322)	1.973(26)
Ti(3)-O(341)	2.049(18)	Ti(3)-O(431)	2.016(27)
Ti(4)-O(34)	1.797(26)	Ti(4)-O(45)	1.811(19)
Ti(4)-O(342)	2.080(18)	Ti(4)-O(432)	1.979(24)
Ti(4)-O(451)	2.059(29)	Ti(4)-O(541)	2.017(23)
Ti(5)-O(45)	1.781(23)	Ti(5)-O(56)	1.788(23)
Ti(5)-O(452)	2.054(24)	Ti(5)-O(542)	2.010(22)
Ti(5)-O(561)	2.039(26)	Ti(5)-O(651)	2.014(21)
Ti(6)-O(56)	1.787(20)	Ti(6)-O(67)	1.847(23)
Ti(6)-O(562)	2.026(26)	Ti(6)-O(652)	2.019(25)
Ti(6)-O(671)	2.043(25)	Ti(6)-O(761)	2.025(25)
Ti(7)-O(67)	1.766(23)	Ti(7)-O(78)	1.820(23)
Ti(7)-O(672)	2.046(25)	Ti(7)-O(762)	1.973(22)
Ti(7)-O(781)	2.077(25)	Ti(7)-O(871)	2.021(24)
Ti(8)-O(78)	1.783(22)	Ti(8)-O(81)	1.828(21)
Ti(8)-O(782)	2.051(22)	Ti(8)-O(872)	1.986(24)
Ti(8)-O(182)	2.091(21)	Ti(8)-O(812)	2.004(26)
O(121)-C(120)	1.257(23)	O(122)-C(120)	1.209(24)
O(211)-C(210)	1.260(24)	O(212)-C(210)	1.240(19)
O(231)-C(230)	1.330(21)	O(232)-C(230)	1.182(30)
O(321)-C(320)	1.319(24)	O(321)-C(320)	1.266(30)
O(341)-C(340)	1.249(27)	O(342)-C(340)	1.264(28)
O(431)-C(430)	1.233(31)	O(432)-C(430)	1.253(27)
O(451)-C(450)	1.286(39)	O(452)-C(450)	1.285(25)
O(541)-C(540)	1.243(26)	O(542)-C(540)	1.249(25)
O(561)-C(560)	1.296(30)	O(562)-C(560)	1.216(27)
O(651)-C(650)	1.228(21)	O(652)-C(650)	1.206(27)

Table 6.2 continued

O(671)-C(670)	1.191(27)	O(672)-C(670)	1.314(31)
O(761)-C(760)	1.225(29)	O(762)-C(760)	1.242(22)
O(781)-C(780)	1.320(37)	O(782)-C(780)	1.197(38)
O(871)-C(870)	1.273(29)	O(872)-C(870)	1.198(29)
O(181)-C(180)	1.281(24)	O(182)-C(180)	1.165(27)
O(811)-C(810)	1.246(28)	O(812)-C(810)	1.227(26)

Table 6.3 Selected bond angles for [{$TiO(O_2CC_6F_5)_2$}8] (°)

O(12)-Ti(1)-O(81)	102.0(10)	O(12)-Ti(1)-O(121)	89.9(9)
O(81)-Ti(1)-O(121)	167.8(8)	O(12)-Ti(1)-O(211)	87.3(9)
O(81)-Ti(1)-O(211)	93.0(10)	O(121)-Ti(1)-O(211)	90.0(9)
O(12)-Ti(1)-O(181)	169.4(10)	O(81)-Ti(1)-O(181)	87.9(9)
O(121-Ti(1)-O(181)	80.4(8)	O(211)-Ti(1)-O(181)	88.3(8)
O(12)-Ti(1)-O(811)	94.3(9)	O(81)-Ti(1)-O(811)	91.8(10)
O(121)-Ti(1)-O(811)	84.7(10)	O(211)-Ti(1)-O(811)	174.5(10)
O(181)-Ti(1)-O(811)	89.2(9)	O(12)-Ti(2)-O(23)	100.0(10)
O(12)-Ti(2)-O(122)	90.8(9)	O(23)-Ti(2)-O(122)	168.9(9)
O(12)-Ti(2)-O(212)	89.9(9)	O(23)-Ti(2)-O(212)	95.4(10)
O(122)-Ti(2)-O(212)	87.2(9)	O(12)-Ti(2)-O(231)	171.2(10)
O(23)-Ti(2)-O(231)	88.4(9)	O(122)-Ti(2)-O(231)	81.0(9)
O(212)-Ti(2)-O(231)	86.6(8)	O(12)-Ti(2)-O(321)	95.2(9)
O(23)-Ti(2)-O(321)	88.5(10)	O(122)-Ti(2)-O(321)	87.9(10)
O(212)-Ti(2)-O(321)	172.9(10)	O(231)-Ti(2)-O(321)	87.7(8)
O(23)-Ti(3)-O(34)	98.7(9)	O(23)-Ti(3)-O(232)	90.9(9)
O(34)-Ti(3)-O(232)	169.3(10)	O(23)-Ti(3)-O(322)	88.9(10)
O(34)-Ti(3)-O(322)	97.5(11)	O(232)-Ti(3)-O(322)	87.4(11)
O(23)-Ti(3)-O(341)	170.9(11)	O(34)-Ti(3)-O(341)	90.3(9)
O(232)-Ti(3)-O(341)	80.3(9)	O(322)-Ti(3)-O(341)	88.4(9)
O(23)-Ti(3)-O(431)	94.5(9)	O(34)-Ti(3)-O(431)	89.6(11)
O(232)-Ti(3)-O(431)	84.9(10)	O(322)-Ti(3)-O(431)	171.6(10)
O(341)-Ti(3)-O(431)	87.0(9)	O(34)-Ti(4)-O(45)	97.9(9)
O(34)-Ti(4)-O(342)	90.9(9)	O(45)-Ti(4)-O(342)	171.1(11)
O(34)-Ti(4)-O(432)	89.3(11)	O(45)-Ti(4)-O(432)	92.0(9)
O(342)-Ti(4)-O(432)	86.8(9)	O(34)-Ti(4)-O(451)	172.4(10)
O(45)-Ti(4)-O(451)	89.0(10)	O(342)-Ti(4)-O(451)	82.1(9)
O(432)-Ti(4)-O(451)	87.3(10)	O(34)-Ti(4)-O(541)	97.3(11)
O(45)-Ti(4)-O(541)	93.6(9)	O(342)-Ti(4)-O(541)	86.5(9)
O(432)-Ti(4)-O(541)	170.7(8)	O(451)-Ti(4)-O(541)	85.3(10)
O(45)-Ti(5)-O(56)	101.2(11)	O(45)-Ti(5)-O(452)	88.1(10)
O(56)-Ti(5)-O(452)	170.7(11)	O(45)-Ti(5)-O(542)	92.9(10)
O(56)-Ti(5)-O(542)	90.2(9)	O(452)-Ti(5)-O(542)	89.9(9)
O(45)-Ti(5)-O(561)	170.5(9)	O(56)-Ti(5)-O(561)	87.7(10)

Table 6.3 continued

O(452)-Ti(5)-O(561)	83.0(10)	O(542)-Ti(5)-O(561)	83.9(10)
O(45)-Ti(5)-O(651)	96.9(10)	O(56)-Ti(5)-O(651)	89.6(9)
O(452)-Ti(5)-O(651)	88.6(9)	O(542)-Ti(5)-O(651)	170.1(11)
O(561)-Ti(5)-O(651)	86.2(9)	O(56)-Ti(6)-O(67)	101.3(10)
O(56)-Ti(6)-O(562)	89.8(9)	O(67)-Ti(6)-O(562)	168.7(10)
O(56)-Ti(6)-O(652)	89.2(10)	O(67)-Ti(6)-O(652)	92.1(10)
O(562)-Ti(6)-O(652)	90.2(10)	O(56)-Ti(6)-O(671)	168.6(12)
O(67)-Ti(6)-O(671)	89.9(10)	O(562)-Ti(6)-O(671)	79.1(9)
O(652)-Ti(6)-O(671)	88.3(10)	O(56)-Ti(6)-O(761)	95.2(10)
O(67)-Ti(6)-O(761)	88.7(10)	O(562)-Ti(6)-O(761)	88.2(10)
O(652)-Ti(6)-O(761)	175.4(9)	O(671)-Ti(6)-O(761)	87.1(10)
O(67)-Ti(7)-O(78)	101.0(10)	O(67)-Ti(7)-O(672)	89.8(10)
O(78)-Ti(7)-O(672)	168.8(9)	O(67)-Ti(7)-O(762)	90.1(9)
O(78)-Ti(7)-O(762)	91.2(10)	O(672)-Ti(7)-O(762)	91.4(10)
O(67)-Ti(7)-O(781)	171.4(11)	O(78)-Ti(7)-O(781)	87.4(10)
O(672)-Ti(7)-O(781)	81.9(10)	O(762)-Ti(7)-O(781)	88.0(9)
O(67)-Ti(7)-O(871)	94.0(10)	O(78)-Ti(7)-O(871)	89.5(10)
O(672)-Ti(7)-O(871)	87.1(9)	O(762)-Ti(7)-O(871)	175.6(9)
O(781)-Ti(7)-O(871)	87.7(10)	O(78)-Ti(8)-O(81)	98.5(9)
O(78)-Ti(8)-O(782)	92.0(10)	O(81)-Ti(8)-O(782)	169.5(10)
O(78)-Ti(8)-O(872)	91.4(10)	O(81)-Ti(8)-O(872)	93.6(10)
O(782)-Ti(8)-O(872)	87.2(9)	O(78)-Ti(8)-O(182)	171.9(9)
O(81)-Ti(8)-O(182)	88.1(9)	O(782)-Ti(8)-O(182)	81.6(9)
O(872)-Ti(8)-O(182)	83.3(9)	O(78)-Ti(8)-O(812)	96.1(10)
O(81)-Ti(8)-O(812)	91.9(10)	O(782)-Ti(8)-O(812)	85.8(9)
O(872)-Ti(8)-O(812)	169.8(9)	O(182)-Ti(8)-O(812)	88.3(9)
Ti(1)-O(12)-Ti(2)	136.6(13)	Ti(2)-O(23)-Ti(3)	136.5(12)
Ti(3)-O(34)-Ti(4)	134.4(13)	Ti(4)-O(45)-Ti(5)	133.2(11)
Ti(5)-O(56)-Ti(6)	136.6(15)	Ti(6)-O(67)-Ti(7)	135.1(14)
Ti(7)-O(78)-Ti(8)	135.1(9)	Ti(1)-O(81)-Ti(8)	135.4(14)
Ti(1)-O(121)-C(120)	130.4(16)	Ti(2)-O(122)-C(120)	130.5(17)
O(121)-C(120)-O(122)	129.4(21)	Ti(1)-O(211)-C(210)	131.9(12)
Ti(2)-O(212)-C(210)	130.9(16)	O(211)-C(210)-O(212)	126.1(18)
Ti(2)-O(231)-C(230)	130.5(16)	Ti(3)-O(232)-C(230)	132.1(15)

Table 6.3 continued

O(231)-C(230)-O(232)	126.9(19)	Ti(2)-O(321)-C(320)	136.5(19)
Ti(3)-O(322)-C(320)	134.0(15)	O(321)-C(320)-O(322)	119.0(20)
Ti(3)-O(341)-C(340)	134.3(16)	Ti(4)-O(342)-C(340)	133.3(15)
O(341)-C(340)-O(342)	122.5(15)	Ti(3)-O(431)-C(430)	134.3(18)
Ti(4)-O(432)-C(430)	135.5(19)	O(431)-C(430)-O(432)	120.3(19)
Ti(4)-O(451)-C(450)	134.8(14)	Ti(5)-O(452)-C(450)	132.0(21)
O(451)-C(450)-O(452)	121.3(21)	Ti(4)-O(541)-C(540)	131.7(15)
Ti(5)-O(542)-C(540)	134.9(18)	O(541)-C(540)-O(542)	124.5(18)
Ti(5)-O(561)-C(560)	133.0(19)	Ti(6)-O(562)-C(560)	130.8(20)
O(561)-C(560)-O(562)	123.1(22)	Ti(5)-O(651)-C(650)	128.1(18)
Ti(6)-O(652)-C(650)	131.5(15)	O(651)-C(650)-O(652)	131.0(19)
Ti(6)-O(671)-C(670)	133.4(22)	Ti(7)-O(672)-C(670)	131.4(14)
O(671)-C(670)-O(672)	126.3(20)	Ti(6)-O(761)-C(760)	132.1(15)
Ti(7)-O(762)-C(760)	132.6(18)	O(761)-C(760)-O(762)	126.3(19)
Ti(7)-O(781)-C(780)	132.3(20)	Ti(8)-O(782)-C(780)	131.8(19)
O(781)-C(780)-O(782)	126.1(24)	Ti(7)-O(871)-C(870)	133.6(17)
Ti(8)-O(872)-C(870)	133.9(17)	O(871)-C(870)-O(872)	125.2(18)
Ti(1)-O(181)-C(180)	128.3(16)	Ti(8)-O(182)-C(180)	130.2(14)
O(181)-C(180)-O(182)	129.9(15)	Ti(1)-O(811)-C(810)	132.1(17)
Ti(8)-O(812)-C(810)	130.9(19)	O(811)-C(810)-O(812)	127.8(20)

One of each pair of bridging pentafluorobenzoate ligands is roughly orientated in the same plane (equatorial) as the titanium atoms, but there is no correlation between the planes of the phenyl rings and this plane. The other pentafluorobenzoate ligand is more or less perpendicular (axial) to this plane so that there are four carboxylate ligands on each side of the plane as can be seen from Figure 6.4.

Despite the high R value (0.140) the primary structure has been established unequivocally with clear evidence for the main solvent molecules. The structure is notable for including a substantial number of toluene molecules, some of which are highly disordered. Each set of four pentafluorobenzoate groups perpendicular to the $[TiO]_8$ plane forms a box which contains one solvent toluene molecule. The total number of toluene molecules in the asymmetric unit is approximated as six from X-ray study. However this is reduced on pumping the crystals overnight under vacuum to give a cream-coloured powder which analyses as $[\{TiO(O_2CC_6F_5)_2\}_8].3C_7H_8$.

The two toluene molecules which are held within the molecule cavity are held by van der Waals contacts with the C_6F_5 units between which they are sandwiched, and also make van der Waals contacts with the oxygen atoms of the Ti-O-Ti linkages (O--C 3.6-3.9Å); the head to head methyl-methyl contact is also fairly short (C--C 3.32Å).

At the titaniums, the angle between bonds to the oxygens of the two equatorial carboxylate oxygens are rather small at about 80°. This is the angle opposite to Ti-O-Ti (100°, referred to above). All other bonds are at or just less than right angle.

The O-C-O carboxylate angles vary from 119.0-131.0° clearly opening up from the ideal 120°. The carboxylate strain is further shown in the Ti-O-C angle which on average is 132.2°.

6.3. Discussion

The reactions carried out by Kapoor and co-workers have been shown in Table 6.1. In each case, the author reported the presence of the respective acyl chloride in the mother liquors, which were distilled and characterised, and suggests that after the formation of $[TiCl_2(O_2CR)_2]$, no further HCl gas is evolved, and the reaction proceeds according to the equation

$$[TiCl_2(O_2CR)_2] + 2RCO_2H \longrightarrow [TiO(O_2CR)_2] + 2RCOCl + H_2O$$

and then

$$RCOCl + H_2O \xrightarrow{v.slow} RCO_2H + HCl$$

From the results gained during the investigations carried out for this thesis it seems very likely that the initial bis-substituted species were misformulated. It has been reported in Chapter 2 that the compounds previously characterised as $[TiCl_2(O_2CR)_2]$ (R=Me, Et, CMe_3) are, in fact, binuclear oxo species containing co-ordinated carboxylic acid molecules of the formula $[\{TiCl_2(O_2CR)(RCO_2H)\}_2O]$ (R=Me, Et, CMe_3). Therefore, the equation above should be modified, as follows.

$$[\{TiCl_2(O_2CR)(RCO_2H)\}_2O] + 4RCO_2H \longrightarrow 2[TiO(O_2CR)_2] + 4RCOCl + 3H_2O$$

Kapoor proposed that the acyl chloride and water occur together as products, and combine to form HCl and the carboxylic acid.[174] In a parallel reaction carried out by Kapoor between acetyl chloride and water at room temperature in the presence of excess acetic acid, the amount of HCl evolved showed that the two combine according to the equation below up to a maximum of about 2% in 24 hours.

$$MeCOCl + H_2O \xrightarrow{MeCO_2H} MeCO_2H + HCl$$

If this reaction is as slow as suggested, then it should be possible to observe the presence of water in the IR spectrum of the reaction liquors. However, observation of the mother liquors after the reaction of pentafluorobenzoic and pentafluorophenylacetic acid with

$TiCl_4$ revealed only the presence of the respective acid chloride. Thus, it would appear that the reaction after the formation of $[\{TiCl_2(O_2CR)(RCO_2H)\}_2O]$ proceeds as follows.

$$[\{TiCl_2(O_2CR)(RCO_2H)\}_2O] + RCO_2H \longrightarrow 2[TiO(O_2CR)_2] + RCOCl + 3HCl$$

In another experiment carried out by Kapoor '$[TiCl_2(O_2CMe)_2]$' was refluxed with excess of *n*-butyric acid. The product corresponded to $[TiO(O_2CMe)_2]$ and not to $[TiO(O_2C^nBu)_2]$ and the mother liquor contained butyryl chloride, thereby confirming that the additional acid provides a further oxo bridge.

It is therefore proposed that the pentafluorobenzoate and pentafluorophenylacetate derivatives of the formula $[TiO(O_2CR)_2]$ are formed by the following equation.

$$TiCl_4 + 3RCO_2H \xrightarrow{\text{Toluene}} [TiO(O_2CR)_2] + 3HCl + RCOCl$$
$$(R=C_6F_5\ ,\ CH_2C_6F_5)$$

In addition to this preparative route, $[TiO(O_2CR)_2]$ ($R=C_6F_5$, $CH_2C_6F_5$) may be prepared, in lower yield (20-30%) by heating the product obtained at room temperature, namely $[\{TiCl_2(O_2CR)(RCO_2H)\}_2O]$ ($R=C_6F_5$, $CH_2C_6F_5$), to reflux in toluene.

It has been discussed that $[\{TiCl_2(O_2CR)(RCO_2H)\}_2O]$ with the carboxylic acid may be heated to produce $[TiO(O_2CR)_2]$ with subsequent formation of the acid chloride and hydrogen chloride gas. It is proposed for this thesis that with the absence of further carboxylic acid, the reaction proceeds by the following route.

$$2[\{TiCl_2(O_2CR)(RCO_2H)\}_2O] \longrightarrow [Ti_4O_2Cl_6(O_2CR)_6] + 2RCO_2H + 2HCl$$

and then further

$$2[\{TiCl_2(O_2CR)(RCO_2H)\}_2O] + 2RCO_2H \longrightarrow 4[TiO(O_2CR)_2] + 2RCOCl + 6HCl$$
$$(R=C_6F_5\ ,\ CH_2C_6F_5)$$

Thus the overall equation may be written as

$$4[\{TiCl_2(O_2CR)(RCO_2H)\}_2O] \xrightarrow{\text{heat}}$$
$$[Ti_4O_2Cl_6(O_2CR)_6] + 4[TiO(O_2CR)_2] + 2RCOCl + 8HCl$$

As yet, there is no evidence for the formation of $[Ti_4O_2Cl_6(O_2CR)_6]$ ($R=C_6F_5$, $CH_2C_6F_5$) but this route could possibly account for the low yield of $[TiO(O_2CR)_2]$.

The formation of $[Ti_4O_2Cl_6(O_2CR)_6]$ is not so unlikely, as the reaction of $TiCl_4$ with benzoic acid at high temperatures has been found to yield this product in quantitative yield.[191]

$$4TiCl_4 + 8PhCO_2H \longrightarrow [Ti_4O_2Cl_6(O_2CPh)_6] + 2PhCOCl + 8HCl$$

Reactions with molar ratios varying from 1:2 to 1:3 were investigated and in each case the above compound was isolated, therefore excess acid had no effect on the product. It may, however, be possible that in the case of a stronger acid such as pentafluorobenzoic or pentafluorophenylacetic acid, further reaction does occur to produce species of the type $[TiO(O_2CR)_2]$.

Closer investigations of these reactions needs to be carried out to establish the exact route for the formation of $[\{TiO(O_2CR)_2\}_8]$ from heating the binuclear species $[\{TiCl_2(O_2CR)(RCO_2H)\}_2O]$ ($R=C_6F_5$, $CH_2C_6F_5$). It may be a simple factor of solubility which enables $[TiO(O_2CR)_2]$ to be precipitated from solution in preference to $[Ti_4O_2Cl_6(O_2CR)_6]$ ($R=C_6F_5$, $CH_2C_6F_5$).

It may also be possible that with the addition of further carboxylic acid, a higher yield of $[TiO(O_2CR)_2]$ ($R=C_6F_5$, $CH_2C_6F_5$) would result, according to the equation below, since in this case, no $[Ti_4O_2Cl_6(O_2CR)_6]$ would be produced.

$$[\{TiCl_2(O_2CR)(RCO_2H)\}_2O] + RCO_2H \longrightarrow 2[TiO(O_2CR)_2] + RCOCl + 3HCl$$

6.4. Preparation of the compound $[Ti_3O_2Cl_4(O_2CCH_2OC_6F_5)_4]$

Continuing with elevated temperature experiments, the reaction of $TiCl_4$ with pentafluorophenoxyacetic acid, $C_6F_5OCH_2CO_2H$, has been investigated. Room temperature experiments carried out for this thesis (Chapter 3) have shown that $C_6F_5OCH_2CO_2H$ gives $[\{TiCl_2(O_2CCH_2OC_6F_5)\}_2O]$ when reacted with $TiCl_4$ whereas

pentafluorobenzoic and pentafluorophenylacetic acids produce [{$TiCl_2(O_2CR)(RCO_2H)$}$_2O$] in an an analogous reaction . This difference in products has been attributed to the presence of an ethereal oxygen in $C_6F_5OCH_2CO_2H$ which has the ability to co-ordinate to a metal centre in addition to the carboxylate moiety. It was therefore of interest to investigate the high temperature reaction between $TiCl_4$ and pentafluorophenoxyacetic acid in order to discover if further reactions may occur to produce a different type of compound, and in addition, to examine whether the ethereal oxygen is still co-ordinated to the titanium metal centre.

We have seen that utilising pentafluorobenzoic and pentafluorophenylacetic acids in high temperature reactions affords the air stable species [$TiO(O_2CR)_2$] (R=C_6F_5, $CH_2C_6F_5$). The product obtained by utilising $C_6F_5OCH_2CO_2H$ may be formulated as [$Ti_3O_2Cl_4(O_2CCH_2OC_6F_5)_4$].0.75$C_6H_6$.0.25$C_6H_{14}$ from elemental analysis, the presence of the solvent molecules further being indicated by the ^{1}H NMR spectrum of the product.

The addition of $TiCl_4$ (1 mol) to a solution of pentafluorophenoxyacetic acid (2.5 mol) in benzene with subsequent heating to reflux, produces the title compound which may be isolated in approximately 50% yield as a crystalline compound by layering the reaction solution with hexane.

The route of formation is proposed to follow the equation below.

$$3TiCl_4 + 6C_6F_5OCH_2CO_2H \longrightarrow [Ti_3O_2Cl_4(O_2CCH_2OC_6F_5)_4] + C_6F_5OCH_2COCl + 6HCl$$

The title compound was characterised by elemental analysis, IR and ^{1}H NMR spectroscopy as outlined below.

IR Spectrum of [$Ti_3O_2Cl_4(O_2CCH_2OC_6F_5)_4$]

Absorption bands at 1584 and 1560cm^{-1} are assigned to $\upsilon(COO)_{asym}$ and bands at 1450 and 1410cm^{-1} are labelled as $\upsilon(COO)_{sym}$. The Δ values are therefore 134 and 140cm^{-1} which would be indicative of bridging carboxylate ligation and are comparable with

the Δ values of 103 and 137cm^{-1} which have been observed in the IR spectrum of [{$TiCl_2(O_2COCH_2C_6F_5)$}$_2$O]. Absorption bands in the region 1300-1000cm^{-1} within which υ(C-O-C) is contained show no change from those present in the IR spectrum of the free acid, therefore indicating that no co-ordination of the etheral oxygen to the metal atom occurs. υ(Ti-O-Ti) is difficult to assign as there are many bands in this region but may be tentatively designated to a band at 718cm^{-1}. The product is air sensitive, indicating the presence of Ti-Cl bonds, and such bonds are also evident from the IR spectrum which exhibits bands at 440, 430, 415 and 390cm^{-1} which may be attributed to terminal υ(Ti-Cl). No bridging Ti-Cl bonds are apparent.

^{1}H NMR Spectrum of $[Ti_3O_2Cl_4(O_2CCH_2OC_6F_5)_4]$

The ^{1}H NMR spectrum of the title compound in d^8-toluene showed a singlet at δ4.30 (8H) which is attributed to the methylene protons of the pentafluorophenoxyacetate ligands. As only a singlet occurs, the protons are equivalent. A signal at δ7.22 is assigned to solvate benzene protons (4.5) and methylene and methyl signals exhibited at δ1.28 and 0.94 are attributed to the presence of solvate hexane (3.5H). The solvent used in the preparation (benzene) and that used in the work-up of the compound (hexane) could not be removed even after pumping the sample for several hours with slight warming. The ^{1}H NMR aggrees with the analytical data, indicating the formulation $[Ti_3O_2Cl_4(O_2CCH_2OC_6F_5)_4].0.75C_6F_5.0.25C_6H_{14}$.

CHAPTER SEVEN

ZIEGLER NATTA CATALYSIS

ALUMINIUM CARBOXYLATE SPECIES

7. INTRODUCTION

7.1 Ziegler-Natta Catalysis

A selection of the titanium compounds which have been synthesised for this thesis was tested at I.C.I., Wilton for their ability to act as Ziegler-Natta catalytic precursors in the polymerisation of propylene. Before these results are presented, a brief overview of the Ziegler-Natta catalytic process is given. More detailed information on this large subject area may be obtained from the many good reviews which have been published.[3]

Karl Ziegler and Guilio Natta revolutionised the polymer industry with the advent of a class of catalysts based on transition metal compounds which could polymerise alkenes and dienes with very high activity and stereoselectivity, at low temperatures and pressures. In many of the areas in which successful Ziegler-Natta catalysts are utilised, a titanium compound is used as a component of the catalyst (e.g. $TiCl_4$ or $TiCl_3$) along with a main group element alkyl halide or alkyl compound such as $AlClR_2$ or AlR_3 (R=alkyl).

7.1.1. Polymeric Structure

Polyethylene, as produced by Ziegler-Natta catalysis, is composed of long chains of CH_2 units containing very few of the branches typical of polyethylene made using free radical catalysts. However with polypropylene three structural types are possible as outlined below in Figure 7.1.

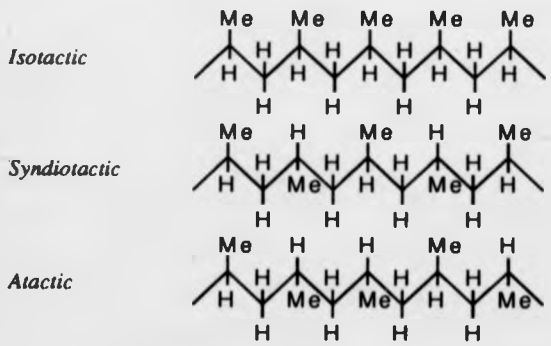


Figure 7.1 Isomers of polypropylene

Propylene polymerisation generally affords a mixture of either syndiotactic or isotactic with atactic polymer. Modifications of the basic catalyst such as structurally altering the components may modify the ratio of stereoregular polymer (atactic or syndiotactic) to that of the 'random' atactic polymer. Their differing structures give varying solubilities and a common test as to the ratio of each polymer type present is to measure the proportion of polymer soluble in certain solvents such as ether, xylene, and heptane. It is industrially desirable for the polypropylene polymer to have a stereoregular structure. Isotactic polypropylene benefits from a higher melting and softening point, which means that it is suitable under a wider range of conditions, and therefore many Ziegler-Natta catalysts are developed to produce this isomer in very high yield.

7.2. The Mechanism of Ziegler-Natta Catalysis

Since the initial discovery of this important class of catalysts in 1952 the mechanism of the catalytic process has not been fully established. Generally, it is believed that the polymerisation process involves the formation of a complex between the alkene and the active site of the catalyst, followed by a propagation step where the added alkene extends the polymer chain.

The main belief is that propagation occurs at a metal-alkyl bond which could be the transition metal alkyl, the activator alkyl, or an alkyl group which is bridging between these two components. The most generally accepted mechanism for alkene polymerisation is that of Cossee and Arlman who suggested that polymerisation occurred at surface titanium atoms which possessed a vacant co-ordination site.[275] The mechanism is shown schematically in Figure 7.2. It proposes that the olefin process is initiated by the alkylated transition metal and after carrying out its alkylation function the aluminium alkyl takes no further part in the reaction. The alkene monomer co-ordinates to the transition metal at the vacant site and the C=C bond is ruptured to form a four-membered cyclic intermediate. The alkyl group is then transferred to the bound alkene which subsequently forms a σ bond to the transition metal

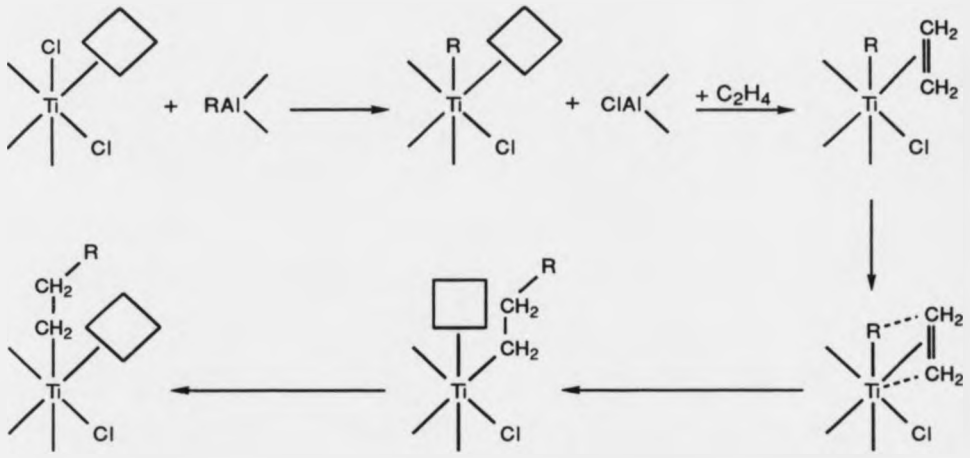


Figure 7.2 Cossee Arlman monometallic mechanism.

atom. The complex then returns to the initial state by exchange of the polymer chain and the vacant site, allowing the polymerisation process to be repeated.

The closest rival to the above mechanism of Cossee and Arlman is that of Rodriguez and van Looy who proposed that the growing polymer chain forms a bridge between the transition metal and the activator alkyl.

Evidence in favour of the active centre being solely the transition metal atom comes from the existence of catalytic systems which polymerise alkenes in the absence of an activator, such as the catalyst [$TiMeCl_3$] / $TiCl_3$. Although the bimetallic site may be the active site in catalysts containing both a transition metal compound and an activator, the monometallic aluminium alkyl active site model is thought to be unlikely.

7.3. Stereoregulation

A successful catalyst in propylene polymerisation is dependent upon its ability to control the stereochemistry of the growth step so that a crystalline, isotactic polymer can be produced. This stereoregulation is proposed as arising as a consequence of the asymmetry of the transition metal site.

Cossee and Arlman tackled the problem of stereoregulation in Ziegler-Natta polymerisation by considering the situation at the lateral surface of α-$TiCl_3$.[276] It was suggested that the titanium atoms are octahedrally co-ordinated with one of the vertices being a vacancy. A terminal chlorine is exchanged for an alkyl moiety and it was assumed that the alkene monomer co-ordinates to the titanium centre at the vacant vertex so that it is orientated parallel to the metal alkyl bond ready for insertion.

With this latter step, four arrangements of the propylene molecule are possible. Cossee and Arlman proposed that the interaction with the surrounding atom is least when the methyl group is furthest away from the surface, Figure 7.3. Thus the orientation of each propylene monomer is fixed and isotactic polypropylene results. Syndiotactic polymerisation can be explained on this model if after one insertion the polymer chain does not migrate back to its original position before a further insertion occurs.

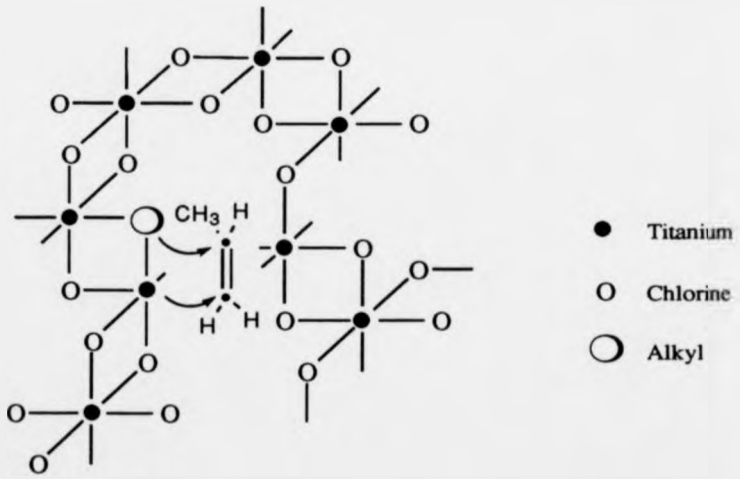


Figure 7.3 Cossee and Arlman proposed that the orientation of each monomer unit is fixed so that stereoregularity occurs.

The history of the development of stereospecific catalysts falls into two main periods. The first period, encompasses the $TiCl_3$-based catalysts originally developed by Natta and co-workers. These are the so-called 'first generation' catalysts and have been

discussed in the previous section. In addition, a large number of 'second generation' catalysts were developed which were based on $TiCl_3$ and modified with organic ligands which behave as Lewis bases. The second period produced highly stereospecific and productive catalysts which are termed 'third generation'. These latter catalysts involve the use of an inert support (such as magnesium chloride) which stems from the observations that the bulk of the titanium sites within the $TiCl_3$ lattice are inactive.

Both the second and third generation catalysts are used extensively in industry today and will now be briefly discussed.

7.4. Propylene Polymerisation Catalysts

7.4.1 Titanium Trichloride Systems

Four crystalline modifications of $TiCl_3$ exist, namely α, β, γ and δ. In all of these forms, the titanium atom is octahedrally co-ordinated by chlorine atoms. In combination with aluminium alkyls all of the above forms of $TiCl_3$ exhibit activity in the polymerisation of propylene although stereoregularity of the polymer varies.

Activity and stereospecificity are also found to differ with the use of different activator molecules. Thus with δ-$TiCl_3$ while a higher activity is found when it was used in combination with $AlEt_3$ than with $AlEt_2X$ (X=halide), the stereospecificity was reduced. Milling a $TiCl_3$ catalyst can further increase the activity which serves to increase the surface area, and hence the number of active sites available.

An increase in both the activity and stereoregularity of the polymer has been achieved by combining Lewis bases with the polymerisation catalyst, either as an additive together with the activator, or as an integral component of the catalyst itself.

A large variety of additives have been used, particularly esters, ethers, and phosphines. Their role may be complex due to their ability to interact with the titanium component or the activator. Among the various proposed functions of the Lewis base the following have been mentioned.

(i) Blocking of the more exposed and less stereospecific active centres by complexing with the titanium atoms at these sites or by increasing steric crowding.

(ii) Complexing and removal of substances which are able to poison the catalysts such as the by-product $AlEtCl_2$.

The effect of the Lewis base on activity is noted even on combination with a $TiCl_3$ catalyst which, in the absence of an activator, would have negligible activity.

7.4.2. Supported ('Third Generation') Catalysts

Only a small number of titanium atoms are ideally situated to behave as active sites. Thus $TiCl_3$ itself may be considered as a 'self-supported' catalyst in which the majority of the titanium atoms are within the bulk of the lattice and therefore inactive. The bulk $TiCl_3$ may be replaced by an inert support, primarily magnesium chloride, with active titanium centres being supported on the exposed surfaces.

The choice of components of a successful supported catalyst for the polymerisation of propylene is limited and in practice a titanium(IV) compound is often used instead of $TiCl_3$. Typically these types af catalyst comprise magnesium chloride, an aromatic ester (e.g. ethyl benzoate) and titanium tetrachloride which is used in conjunction with a trialkylaluminium compound combined with another aromatic ester (e.g. $AlEt_3$ with ethyl anisate). Magnesium chloride has so far proven to be the best support. This unique ability is suggested to be a consequence of the similarity between its crystal structure (ccp) and that of α-$TiCl_3$ (hcp) and γ-$TiCl_3$ (ccp); all are layer lattice structures.

Milling of the magnesium chloride increases the surface area and creates disorder and defects in the lattice. Titanium tetrachloride is then absorbed onto the surface giving a monolayer of active titanium sites. No other support for $TiCl_4$ functions as well as $MgCl_2$ which is possibly a consequence of the compatibility of the ionic radii of Ti^{4+} and Mg^{2+} which are very similar at 0.68 and 0.65Å respectively.

If a Lewis base such as an ester is present when the $MgCl_2$ is milled, the surfaces are rapidly complexed, thus preventing the reagglomeration of the $MgCl_2$ particles and

increasing the activity of the system even further. Although this may be achieved with a variety of Lewis bases, high stereospecificity in particular is only achieved by utilising aromatic esters, which may be used in the catalyst preparation and also as polymerisation additives. The most successful results have been obtained with the use of the methyl and ethyl esters of benzoic, toluic or anisic acids. The reason for the success of these particular systems remains obscure but may well be associated with their ability to impose a favourable steric and electronic arrangement at the active titanium centre.

7.5. CATALYTIC RESULTS AND DISCUSSION

Some of the titanium compounds prepared for this thesis were tested for their catalytic properties in the polymerisation of propene. These tests were carried out at I.C.I. (Wilton). Unfortunately, only a limited number of investigations were able to be carried out, but the results serve to demonstrate that the activity of the compounds, when supported on magnesium chloride is significantly higher than when unsupported in solution.

All the tests, unsupported and supported, were carried out utilising triethylaluminium as the activator. The following method was carried out to examine the catalytic properties of the titanium compounds when unsupported in solution.

7.5.1. Solution Catalysis

A given weight of the titanium compound was dissolved in dry toluene in a Schlenk tube. Propene gas was then added for 10 minutes to allow both the solution and the Schlenk atmosphere to become saturated. Triethylaluminium (1M solution in EC180) was then added and the solution was stirred under a propene atmosphere at room temperature for 1 hour. The reaction product was then poured into methanol to precipitate the polymer and 2.5M sulphuric acid was added. The mixture was then filtered, the residue being washed with methanol and dried.

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Individual experimental details are given in Chapter 8. The results of these investigations will now be discussed.

Solution Catalytic Test Results

The results are summarised in Table 7.1 below.

Table 7.1 Results of the solution catalytic tests of some titanium compounds prepared for this thesis.

Compound	Al:Ti mole ratio	Polymerisation Conditions Temp(^{o}C)/atm/time(h)	Yield of polymer g/mmol Ti
$[\{TiCl_2(O_2CCH_2OC_6F_5)\}_2O]$ **I**	3:1	24/1/1	0.06
$[\{TiCl_2(O_2CEt)(EtCO_2H)\}_2O]$ **II**	13:1	24/1/1	nil
$[\{TiCl_2(O_2CC_6F_5)(C_6F_5CO_2H)\}_2O]$ **III**	12:1	24/1/1	0.13
$[\{TiOCl(O_2CCMe_3)THF\}_4O]$ **IV**	36:1	24/1/1	nil

As is apparent from Table 7.1 the compounds tested by this method were either inactive or only weakly active as catalyst components in the polymerisation of propene. The presence of two *cis* chlorine atoms is thought to be a requirement for catalytic activity. Compounds I, II and III are all proposed as having *cis* chlorine atoms, however, compound II, $[\{TiCl_2(O_2CEt)(EtCO_2H)\}_2O]$, appears to be inactive. Compound IV, as we have seen in Chapter 4 has a cyclic struture with only one terminal atom on each titanium which lends support to the above proposal.

At present it is not known why the pentafluorobenzoate derivative III is active, and the propanoate species II is not. It may be reasonable to assume that the presence of an electron withdrawing group (C_6F_5) may enhance the electrophilic nature of the titanium centre, thus aiding the attack by the alkene to the polymerisation centre. It is interesting to note that the increase in the size of the alkyl group (C_6F_5 *c.f.* C_2H_5) does not appear to hinder sterically the polymerisation process.

7.5.2. Heterogeneous Catalysis

Although activities described in the previous section are low in comparison to commercial catalysts under the same conditions it is well known that the catalytic activity of the titanium compounds in the polymerisation of propene can be considerably enhanced by adsorbing the complex onto magnesium chloride. The following method outlines the process carried out to examine the catalytic properties of the titanium compounds in a heterogeneous system.

The titanium complex and magnesium chloride were suspended in toluene in a Schlenk tube and stirred for 3 hours after which time the toluene was then removed and the precipitate was then washed with EC180. The precipitate was then resuspended in EC180 and propene gas was then added for 10 minutes to allow both the solution and the atmosphere in the Schlenk tube to become saturated. Triethylaluminium was then added and the mixture stirred under a propene atmosphere at room temperature for 1 hour. The liquor was then syringed off to which 2.5M H_2SO_4 was then carefully added to dissolve any alumina. Two layers then formed, and the organic layer was added to acetone to precipitate the polymer which was subsequently filtered, washed and dried.

Individual experimental details are given in Chapter 8. The results of these investigations will now be discussed.

Heterogeneous Catalytic Test Results

The results are summarised in Table 7.2.

A comparison of Tables 7.1 and 7.2 serves to demonstrate that the activity of the titanium carboxylate species tested is considerably enhanced by supporting them on magnesium chloride.

As is indicated from Table 7.2 only the species $[\{TiOCl(O_2CCMe_3)THF\}_4O]$ failed to be an active precursor. This compound also produced no polymer in the solution catalysis

experiments which has been attributed to the absence of *cis* chlorine atoms in the carboxylate compound.

Table 7.2 Results of the heterogeneous catalytic tests of some titanium compounds prepared for this thesis.

Compound	Polymerisation Conditions Temp(°C)/atm/time(h)	Yield of polymer g/g $MgCl_2$
$[\{TiCl_2(O_2CCH_2OC_6F_5)\}_2O]$ I	24/1/1	0.12
$[Ti_2OCl_3(O_2CEt)_3(EtCO_2H)]$ II	24/1/1	0.21
$[\{TiCl_2(O_2CC_6F_5)(C_6F_5CO_2H)\}_2O]$ III	24/1/1	1.07
$[\{TiOCl(O_2CCMe_3)THF\}_4O]$ IV	24/1/1	nil
$[\{Ti_2Cl_7(O_2CEt)(EtCO_2H)\}_4O]$ V	24/1/1	1.89

The other compounds however, are known to have *cis* chlorine atoms. $[Ti_2Cl_7(O_2CEt)(EtCO_2H)]$ appears to be the most active species when supported on magnesium chloride which may possibly be a consequence of the larger chlorine : titanium ratio in this compound. Again the pentafluorobenzoate ligands do not appear to greatly hinder the polymerisation process as some activity is observed.

The results obtained are merely a qualitative measure of the effect of supporting the titanium carboxylate species on magnesium chloride in comparison to the unsupported solution experiments. Since only a small range of compounds have been examined and it is known that many other structural factors could influence the catalytic activity, it is clearly not possible to draw substantive conclusion from these results. However, some general comments on the overall process can be made as follows.

The magnesium chloride which was utilised underwent sonic vibrations for 2 days to reduce the particle size. This was undertaken for convenience instead of ball milling, although it was appreciated that ball milling the compound would have produced a larger surface area leading to a larger amount of the titanium complex being adsorbed and hence an increase in the activity of the catalyst. Only a small amount of the titanium complex is

actually adsorbed onto the surface of the magnesium chloride, as is apparent from the intense colour of the liquor after stirring the components together for 3 hours. Perhaps this time scale should be increased as this could probably increase the activity. Ideally, experiments could be developed to enable the amount of titanium species which is adsorbed onto the magnesium chloride surface to be established. Thus the activity may then be represented in mmol of adsorbed titanium and this would be a better representation of the activity, even allowing for the fact that there is not a simple relationship between the amount of titanium adsorbed and the number of active sites where the polymerisation is actually taking place.

Unfortunately, no tests were carried out on the polymers produced to give an indication of the stereoregularity. Only very small amounts of product were formed which excluded the possibility of NMR and solubility tests.

However, this short section has shown that some of the titanium carboxylate species have the ability to act as active catalyst components in the polymerisation of propene, particularly when supported on a magnesium chloride surface. It would be interesting if this work could be extended and carried out on a larger scale with optimum conditions. Modelling of titanium compounds on magnesium chloride surfaces is seen as an important stage in the formation of highly active Ziegler-Natta catalysts. A large range of information gained from similar such experiments would enable a better understanding of the Ziegler-Natta catalytic mechanism to be obtained, and as a consequence, could aid the design of an 'ultimate' catalytic precursor

7.6. ALUMINIUM CARBOXYLATE SPECIES

We have seen throughout the previous chapters, the preparation and structural characterisation of a variety of titanium carboxylate species from the reaction of $TiCl_4$ and carboxylic acids in various reactant ratios over a range of temperatures. It has been observed from structural determination of some of these compounds that the bridging co-ordination mode of the carboxylate ligand appears to be predominant. Some of the titanium carboxylate species have been found to be catalytically active in the polymerisation of propylene when combined with an aluminium alkyl. Addition of the aluminium alkyl to the titanium carboxylate could possibly result in the formation of heterobinuclear carboxylate species, which serve as the catalyst. In this case the titanium-carboxylate, bonds may break and subsequently reform to bond with the aluminium centre, thus bridging the two metal atoms.

It was therefore considered advantageous to study the synthesis of aluminium carboxylate species as a basis for possibly preparing titanium and aluminium containing carboxylate compounds. The preparative chemistry of aluminium carboxylates has been widely persued, but the structural features of these compounds have not been determined in the majority of cases. It was therefore proposed that some of this earlier work should be extended in the hope of fully characterising the reaction products by X-ray diffraction.

Aluminium chloride was chosen as the starting material in the present study. It has reportedly the ability to react with carboxylic acids to produce mono-, bis-, and tris-substituted compounds *via* the following equation.[277]

$$AlCl_3 + nRCO_2H \longrightarrow [AlCl_{3-n}(O_2CR)_n] + nHCl$$

(R= fatty acid anion; n=1-3)

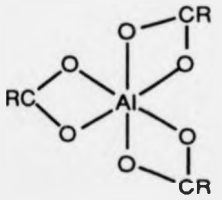
Both $AlCl_3$ and the resultant carboxylates are air sensitive, therefore similar procedures to those utilised in the preparation of the titanium carboxylate species were used. The synthetic reactions which will be reported are only in the initial stages of investigation and, as yet, no structural determination by diffraction methods has been successful despite the high crystallinity of the compounds.

As an introduction to this section, there will will be a brief survey of the synthesis of aluminium carboxylate species to date. Although not entirely comprehensive, it will serve to point out the structural uncertainty which shrouds this area of aluminium chemistry.

7.6.1. A Brief Introduction to Aluminium Carboxylate species

Although the chemistry of aluminium carboxylates has been pursued extensively, very few structures of these compounds have been determined unequivocally from X-ray studies. Work to date has been briefly reviewed.[278,111b]

Early work concerning aluminium carboxylate species centred on the preparation of the monomeric tricarboxylates utilising higher carboxylic acids such as lauric ($C_{11}H_{23}CO_2H$), palmitic ($C_{15}H_{31}CO_2H$) and stearic ($C_{17}H_{35}CO_2H$) acids.[277] Ebullioscopic measurements of the molecular weights of the trisoaps in benzene showed them to be monomolecularly dispersed. On this basis bidentate chelating carboxylate ligation was proposed by Mehrotra and Rai.[279] In these cases the aluminium attains a stable co-ordination number of six.



(7.1)

Various routes to the trisoaps have been claimed, such as those in the following schemes.

$$AlMe_3 + 3RCO_2H \longrightarrow [Al(O_2CR)_3] + 3CH_4$$ [280]

$$Al(O^iPr)_3 + 3RCO_2H \longrightarrow [Al(O_2CR)_3] + 3^iPrOH$$ [281]

The lower carboxylates of aluminium (acetate, propanoate and butyrate) have been synthesised from the addition of the respective anhydride to an aluminium alkoxide.[282]

$$Al(OR)_3 + 3(R'CO)_2O \longrightarrow [Al(O_2CR')_3] + 3R'COOR$$

(R=Et or ^{i}Pr; R'=Me, Et, Bu)

Additionally, anhydrous aluminium trichloride has been reported to react with a mixture of acid anhydride and the corresponding acid to yield the corresponding tri-carboxylate.[283]

$$AlCl_3 + \underset{\text{(Excess)}}{(RCO)_2O} + \underset{\text{(Excess)}}{RCO_2H} \longrightarrow [Al(O_2CR)_3] + 3HCl$$

(R=Me, Et)

Aluminium tricarboxylates as well as chloride carboxylates have been prepared using higher carboxylic acids by refluxing a mixture of anhydrous aluminium chloride and carboxylic acid in benzene solution.[277]

$$AlCl_3 + nRCO_2H \xrightarrow{\text{Benzene}} [AlCl_{3-n}(O_2CR)_n] + nHCl$$

(where n=1, 2, 3 ; R=$C_{11}H_{23}$, $C_{15}H_{31}$, $C_{17}H_{35}$)

Mixed alkoxy carboxylates have been obtained by performing the following reaction in molar ratios of 1:1 and 1:2.

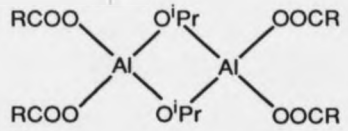
$$Al(O^iPr)_3 + nRCO_2H \xrightarrow{\text{Benzene}} [Al(O^iPr)_{3-n}(O_2CR)_n] + n^iPrOH$$

(where n=1 or 2)

Measurements of the molecular weights of alkoxide **(7.2)** and **(7.3)** and chloride **(7.4)** and **(7.5)** soaps have shown them to be dimeric and trimeric respectively as shown diagramatically overpage.[111b]

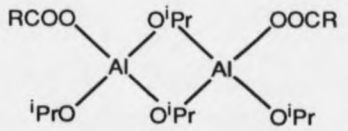
The mixed monoisopropoxide bis-carboxylates of aluminium on heating under reduced pressure yield oxo carboxylates and esters.[284]

$$[Al(O^iPr)(O_2CR)_2] \xrightarrow{\text{heat}} [AlO(O_2CR)] + RCOO^iPr$$



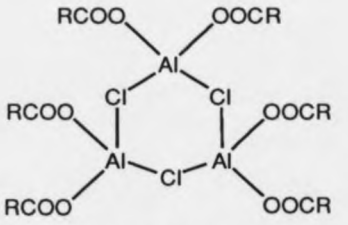
$[\{Al(O^iPr)(O_2CR)_2\}_2]$

(7.2)



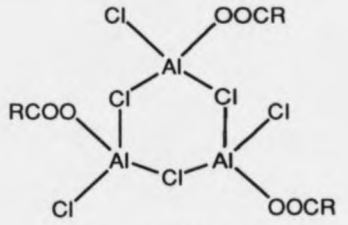
$[\{Al(O^iPr)_2(O_2CR)\}_2]$

(7.3)



$[\{AlCl(O_2CR)_2\}_3]$

(7.4)



$[\{AlCl_2(O_2CR)\}_3]$

(7.5)

These oxide carboxylates, whose structures are unknown, are highly soluble in organic solvents and exhibit a degree of polymerisation of 9-10 in benzene which is reminiscent of the octameric titanium carboxylate $[\{TiO(O_2C_6F_5)_2\}_8]$ which has been discussed in Chapter 6.[284] It was suggested that these species might have either a ring structure or a chain structure but no structural determination has so far been successfully carried out to confirm this proposal.

The oxo species have been prepared more conveniently *via* the following route.

$$[Al(O^iPr)_2(O_2CR)] + H_2O \xrightarrow[\text{benzene}]{\Delta} [Al(O^iPr)(OH)(O_2CR)] + {}^iPrOH$$

$$[Al(O^iPr)(OH)(O_2CR)] \xrightarrow{\sim 170^oC} [AlO(O_2CR)] + {}^iPrOH$$

On heating, aluminium triacetate undergoes decomposition with the loss of acetic anhydride at about 120-140°C and gets converted to the oxyacetate at about 200°C.[285]

$$2[Al(O_2CMe)_3] \xrightarrow{120\text{-}140^oC} [Al_2O(O_2CMe)_4] + (MeCO)_2O$$

$$[Al_2O(O_2CMe)_4] \xrightarrow{\sim 200^oC} 2[AlO(O_2CMe)] + (MeCO)_2O$$

In view of the extreme susceptibility of aluminium derivatives to hydrolysis, non-aqueous media appear to be essential for the preparation of carboxylate species. Indeed in the preparation of tricarboxylates, $[Al(OH)_{3-n}(O_2CR)_n]$ ($n \leq 2$) may be obtained from aqueous solutions.

Very few aluminium carboxylate species have been fully structurally characterised. In an interesting reaction between tetramethylammonium acetate and trimethylaluminium in a 1:2 ratio respectively the following products are present in solution.[286,287]

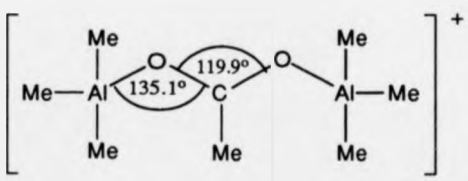
$$[NMe_4][Al_2Me_6(O_2CMe)]_{\text{aromatic}} \rightleftharpoons [NMe_4][AlMe_3(O_2CMe)] + AlMe_3 + \text{aromatic}$$

(7.6) **(7.7)**

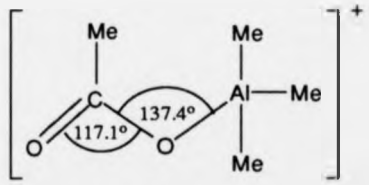
In benzene, the above equilibrium lies to the left but it has been reported that for other aromatic solvents the equation lies progressively farther to the right in the order

benzene < toluene < ethylbenzene < *o*-xylene < *p*-xylene < *m*-xylene

Thus crystals of **(7.6)** have been isolated from toluene solution,[286] and crystals of **(7.7)** from *p*-xylene.[287]



(7.6)



(7.7)

For both of the above compounds the aluminium is in a tetrahedral environment. However, for the 2:1 species an *anti-anti* bridging configuration for the acetate ligand is adopted, most probably due to steric factors involving the methyl ligands. The 1:1 complex, in contrast, exhibits monodentate carboxylate ligation.

A binuclear species has been isolated by Sobota and co-workers which contains a $[Al_2(\mu_2\text{-}OH)(\mu_2\text{-}O_2CMe)_2]^{3+}$ core. $[Al_2(OH)(O_2CMe)_2(MeCO_2Et)_6][AlCl_4]_3$ has been isolated as a hydrolysis product of the compound $[AlCl_2(MeCO_2Et)][AlCl_4]$ during recrystallisation.[288] No scheme or mechanism was suggested for this conversion. The

carboxylate ligands in this example are all bridging and support a μ_2-OH bridge which subtends an angle of 114.8°.

7.7. Preparation of Aluminium Carboxylate species

The initial reactions of $AlCl_3$ with carboxylic acids were carried out utilising propanoic and trimethylacetic acids. Both acids on reaction with $AlCl_3$ at room temperature appeared to give the species $[AlCl_2(O_2CR)]$ (R=Et, CMe_3) which were indicated by elemental analysis.

7.7.1. Preparation of the compounds $[AlCl_2(O_2CR)]$ (R=Et, CMe_3)

A solution of RCO_2H (R=Et, CMe_3) (1 mol) in chloroform was added to a suspension of $AlCl_3$ (1 mol) also in chloroform, at room temperature. After heating to 50°C for 2 hours, the clear yellow solution was then filtered and petroleum ether was added to the filtrate with stirring. The resultant product then precipitated after cooling at -10°C for one week. Air sensitive crystalline products may be isolated for both R=Et and CMe_3 which analyse as $[AlCl_2(O_2CR)]$ and are formed in 65-72% yield according to the following equation.

$$AlCl_3 + RCO_2H \xrightarrow[CHCl_3]{50°C/2hrs} [AlCl_2(O_2CR)] + HCl$$
$$(R=Et, CMe_3)$$

Both compounds are soluble in halogenated and aromatic solvents.

The species $[AlCl_2(O_2CR)]$ (R=Et, CMe_3) were further characterised by IR and ^1H NMR spectroscopy, which will now be discussed.

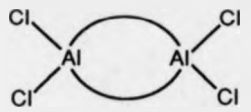
IR and ^1H NMR Spectra of $[AlCl_2(O_2CEt)]$ and $[AlCl_2(O_2CCMe_3)]$

The IR spectra of the title compounds was examined in the region 4000-400cm^{-1}. The $\upsilon(COO)_{asym}$ carboxylate vibration may be assigned to bands at 1575 (R=Et) and 1587cm^{-1} (R=CMe_3), while bands at 1470 (R=Et) and 1460cm^{-1} (R=CMe_3) are attributed to

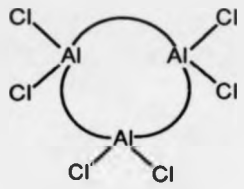
$\upsilon(COO)_{sym}$. Thus the values of Δ [$\upsilon(COO)_{asym}$-$\upsilon(COO)_{sym}$] are 105 (R=Et) and 127cm^{-1} ($R=CMe_3$) which are indicative of the presence of bidentate chelating and / or bridging carboxylate ligands.

The ^1H NMR spectra of [$AlCl_2(O_2CEt)$] shows a quartet centred at δ2.86 and a triplet centred at 1.33 which are attributable to the methylene and methyl protons respectively of the propanoate ligand. Similarly, [$AlCl_2(O_2CCMe_3)$] exhibits a singlet at δ1.37 due to the methyl protons. The spectra would tend to suggest the presence of only one type of carboxylate ligand. From the IR spectra of both compounds the Δ values indicate that no monodentate carboxylate ligands are present. Some possible structures for the compounds [$AlCl_2(O_2CR)$] ($R=Et, CMe_3$) are shown below in Figure 7.4.

Bridging carboxylates



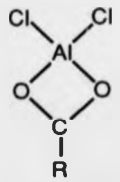
a) Dimeric



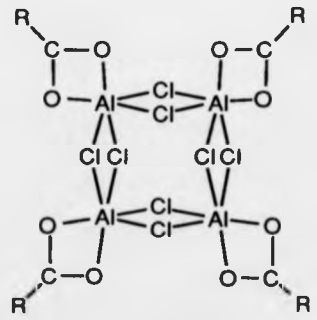
b) Trimeric

Plus other cyclic arrangements

Bidentate chelating carboxylates



c) Monomeric



d) Cyclic

Figure 7.4 Possible structures for the compounds of the formula [$AlCl_2(O_2CR)$] ($R=Et, CMe_3$)

It would at this stage be advantageous to carry out ebullioscopic measurements on the compounds $[AlCl_2(O_2CR)]$ (R=Et, CMe_3) in solution to enable the molecular weight of the species and hence the degree of association, to be calculated. Previous such measurements on species of the type $[AlCl_2(O_2CR)]$ and $[AlCl(O_2CR)_2]$ (R=fatty acid carboxylate) have shown both structures to be trimeric in solution.[111b] Monomeric carboxylate ligation was proposed in these latter compounds.

From the results gained for this thesis it does not seem likely that monomeric carboxylate ligands are present in $[AlCl_2(O_2CR)]$ (R=Et, CMe_3). However, it may be possible that with fatty acid complexes containing much longer carbon chains, a different structure exists, such as those shown previously, **(7.4)** and **(7.5)**.

7.7.2. Preparation of $[AlCl(O_2CEt)_2]$

On increasing both the reactant ratio and the reaction temperature, further substitution occurs when $AlCl_3$ is reacted with propanoic acid. Thus addition of a solution of $EtCO_2H$ (2 mol) in toluene, to a solution of $AlCl_3$ (1 mol) also in toluene with subsequent heating to reflux, affords the disubstituted product $[AlCl(O_2CEt)_2]$ in very high yield (90%) according to the equation below.

$$AlCl_3 + 2EtCO_2H \xrightarrow[\text{Toluene}]{110^{\circ}C} [AlCl(O_2CEt)_2] + 2HCl$$

The colourless product is air sensitive, and has been characterised by IR and ^1H NMR spectroscopy in addition to elemental analysis.

IR and ^1H NMR Spectra of the compound $[AlCl(O_2CEt)_2]$

The bands listed in Table 7.3 may be assigned to the carboxylate absorption bands $\upsilon(COO)_{asym}$ and $\upsilon(COO)_{sym}$. The region 1700-1300cm^{-1} of the IR spectrum for the title compound is shown in Figure 7.5 overleaf.

Table 7.3 Carboxylate absorption bands (cm^{-1}) found in the IR spectrum of $[AlCl(O_2CEt)_2)]$.

$\upsilon(COO)_{asym}$	$\upsilon(COO)_{asym/sym}$	$\upsilon(COO)_{sym}$
1636		1480
1604	1555	1470
1568		1463

Figure 7.5 IR spectrum of $[AlCl(O_2CEt)_2]$ in the region 1800-1000cm^{-1}.

The band situated at 1568cm^{-1} has a slight shoulder at 1555cm^{-1} which may possibly be attributed to a further carboxylate absorption band. This band could be assigned to either $\upsilon(COO)_{asym}$ or $\upsilon(COO)_{sym}$. If it is a symmetric carboxylate stretching band then the maximum value of Δ calculated from this would be 81cm^{-1} (1636-1555cm^{-1}). This value of Δ would tend to indicate the presence of a bridging or a bidentate chelating carboxylate ligand, but as lower Δ values have often been indicative of bidentate chelating modes then it may possibly be assigned to the latter. Additionally, if the band at 1555cm^{-1} is attributable to $\upsilon(COO)_{asym}$ then the maximum value of Δ when paired with a $\upsilon(COO)_{sym}$ band would be 92cm^{-1} (1555-1463cm^{-1}). Again this low value would possibly indicate the presence of bidentate chelating carboxylate ligands. The remaining values of $\upsilon(COO)_{asym}$ and $\upsilon(COO)_{sym}$ which are displayed in Table 7.3 may pair in a variety of combinations to give Δ values of >100cm^{-1}. The maximum possible Δ value is 1636-1463=173cm^{-1} which would still tend to eliminate the presence of unidentate ligation. In summary, it could tentatively be assigned that both bridging and bidentate chelating carboxylate ligands are present in $[AlCl(O_2CEt)_2]$ based on IR data.

Further structural information may be gained from the ^1H NMR spectrum of this species which is shown in Figure 7.6. $[AlCl(O_2CEt)_2]$ exhibits two quartets centred at δ2.57 and 2.37 and two triplets centred at δ1.24 and 1.08 which are attributed to the methylene and methyl protons respectively of the propanoate ligand. This would possibly imply the presence of two types of carboxylate groups in the molecule which may be either spatially inequivalent or of differing co-ordination modes. However, in the titanium species $[Ti_3O_2Cl_3(O_2CCMe_3)_5]$ which has been reported in Chapter 4, a 2:2:1 ratio of methyl siganals is observed due to the spatial arrangement of the ligands in the molecule. The separation between the three singlets is δ0.03 and 0.05. In contrast, for $[AlCl(O_2CEt)_2]$ the separation between two sets of quartets and triplets is considerably larger at δ0.2 and 0.16 respectively. This would therefore possibly suggest that the propanoate (^-O_2CEt) ligands have two co-ordination modes. As the IR spectrum of $[AlCl(O_2CEt)_2]$ has eliminated the possibility of unidentate ligation it is therefore possible that both chelating and bridging

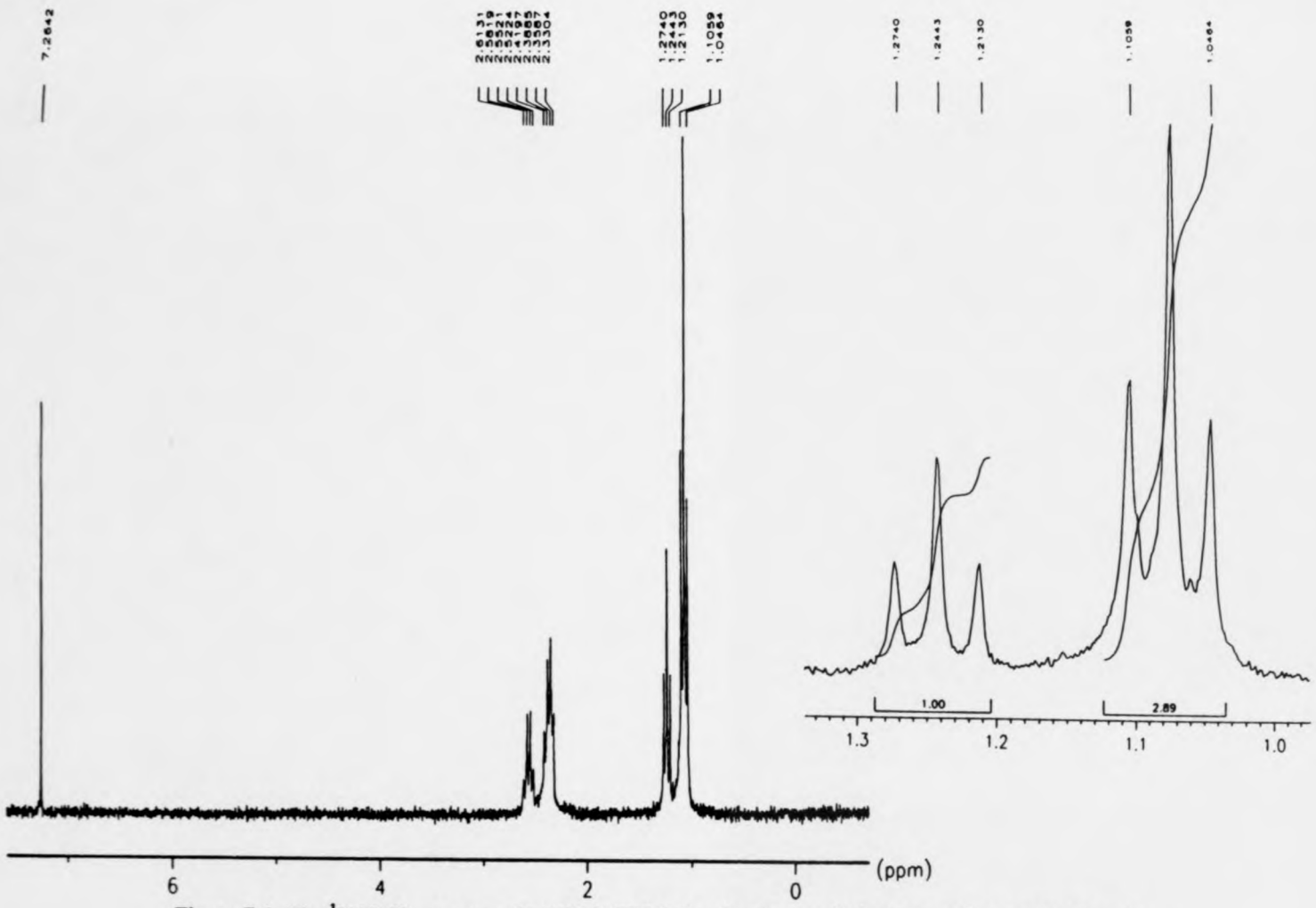


Figure 7.6 The ^{1}H NMR spectrum of $[AlCl(O_2CEt)_2]$ showing the two distinct types of propanoate ligands.

bonding modes exist in the carboxylate. Some possible structures for $[AlCl(O_2CEt)_2]$ are shown in Figure 7.7.

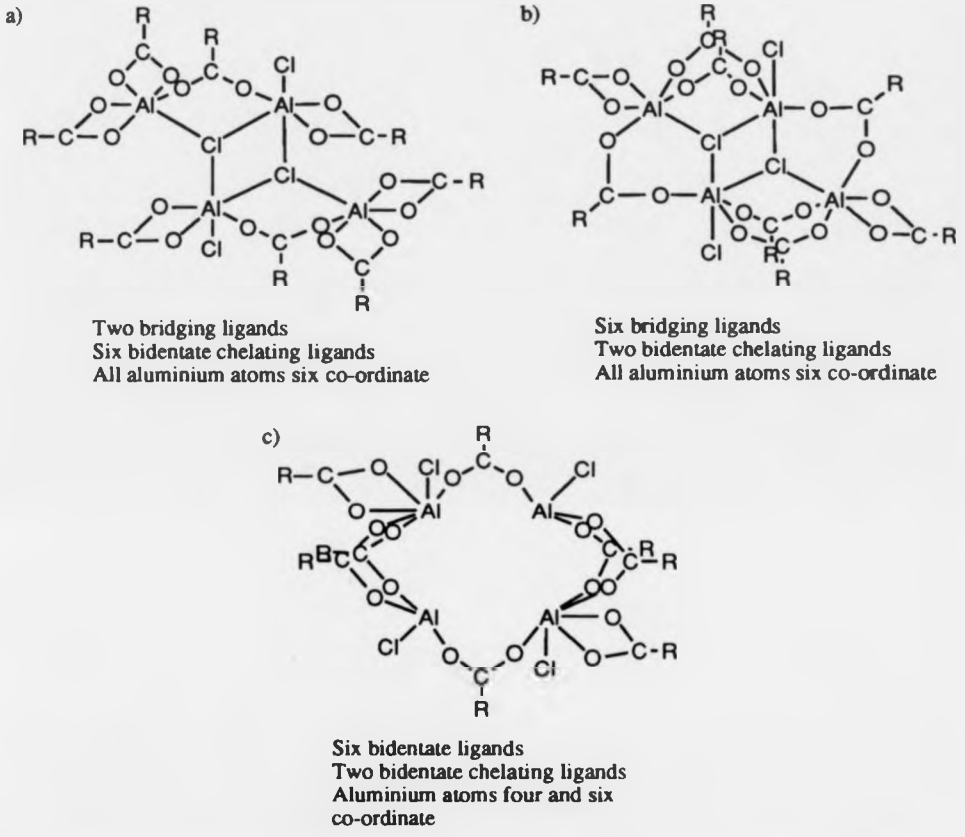


Figure 7.7 Some possible structures for the compound $[AlCl(O_2CEt)_2]$.

7.7.3. Preparation of $[Al(OH)(O_2CPh)_2]$

During these initial investigations, the reaction of $AlCl_3$ with benzoic acid, $PhCO_2H$, was carried out at high temperature, from which, a product was obtained corresponding on analysis to $[Al(OH)(O_2CPh)_2]$. The product is thought to have occurred *via* a hydrolysis reaction. The source of the moisture has been traced to the acetonitrile solvent which was used. Thus, on addition of a solution of benzoic acid (2 mol) in acetonitrile, to a solution of

$AlCl_3$ (1 mol) also in acetonitrile, with subsequent refluxing for 2 hours, the colourless precipitate $[Al(OH)(O_2CPh)_2]$ was produced in high yield according to the equation below.

$$AlCl_3 + 2PhCO_2H + H_2O \longrightarrow [Al(OH)(O_2CPh)_2] + 3HCl$$

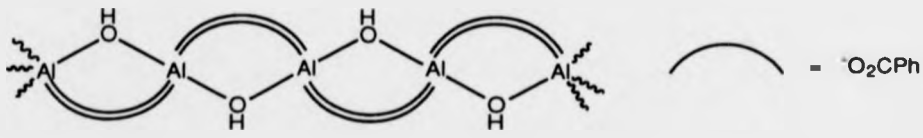
The product is believed to be polymeric on account of its low solubility in a range of organic solvents. In addition to elemental analysis the solid was charcterised by IR spectroscopy.

IR Spectrum of $[Al(OH)(O_2CPh)_2]$

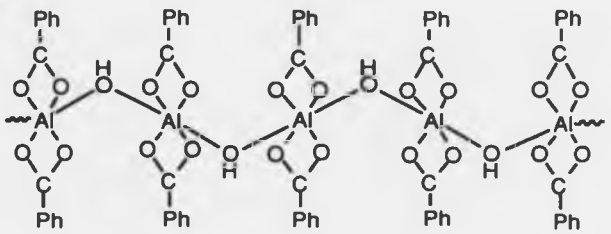
The IR spectrum of the title compound has been previously published by Smirnov *et al.*[289] The authors suggested that the compound was of the formulation $[Al(OH)(O_2CPh)_2.0.5H_2O]$ due to the presence of a broad band centred at 3420cm^{-1} which was assigned as $\upsilon(H_2O)$. The IR spectrum recorded for this thesis is very similar to that of the published spectrum, however, no broad band has been found in the region 3500-3200cm^{-1} and elemental analysis does not support the presence of further hydrogen atoms. A sharp weak intensity band is observed at 3676cm^{-1} which is attributed to $\upsilon(OH)$. This has also been identified in the above publication, and has further been exhibited in the IR spectrum of the carboxylate $[Al_2(\mu_2\text{-}OH)(\mu_2\text{-}O_2CMe)_2(MeCO_2Et)_6][AlCl_4]_3$ at 3600cm^{-1}.

The absorption bands corresponding to $\upsilon(COO)_{asym}$ and $\upsilon(COO)_{sym}$ are found at 1562 and 1440cm^{-1} respectively giving a Δ value of 122cm^{-1} which would be indicative of bidentate chelating and / or bridging carboxylate ligands. Due to only one set of carboxylate absorptions being present and the polymeric nature of the species either of the following structures may be proposed.

a)



b)



Unfortunately, due to the high insolubility of the compound, ^{1}H NMR studies were unable to be carried out.

CHAPTER EIGHT

EXPERIMENTAL

8. EXPERIMENTAL CONDITIONS

The compounds prepared and studied for this thesis are principally moisture sensitive. Manipulations were therefore carried out in an atmosphere of dry inert nitrogen gas, utilising standard Schlenk techniques and a nitrogen filled glove box. See page 238.

Purification and Drying of Solvents and Reagents

The following methods were employed:

Chlorinated solvents : CH_2Cl_2, $CHCl_3$ and CCl_4 were all supplied by Fisons Ltd and distilled from CaH_2 prior to use.

Petroleum ethers : B.p. 60-80°C fraction was supplied by Fisons Ltd; B.p.100-120°C fraction was supplied by May and Baker Ltd. Both were stored over sodium wire and distilled from calcium hydride before use. *Unless specifically stated all petroleum ether used was b.p. 60-80°C.*

n-Hexane : Supplied by Fisons Ltd, was stored over sodium wire and distilled from calcium hydride before use.

Aromatic solvents : Benzene was supplied by May and Baker Ltd, toluene was supplied by Fisons Ltd. Both were stored over sodium wire and distilled from sodium metal prior to use.

Acetonitrile : Supplied by Rathburn Chemicals Ltd and distilled from calcium hydride prior to use.

Tetrahydrofuran : Supplied by Fisons Ltd, stored over sodium wire and distilled from sodium benzophenone ketal before use.

Carboxylic acids and anhydrides : Acetic acid and the anhydride were supplied by Fisons Ltd; propanoic and trimethylacetic acids and the anhydrides were supplied by Aldrich Chemical Company, Inc. Each acid was dried by distilling from an acid / anhydride mix of 90 / 10 ratio.

Pentafluorobenzoic acid, pentafluorophenylacetic acid and pentafluorophenoxyacetic acid were all supplied by Aldrich Chemical Company, Inc. Benzoic acid was supplied by

May and Baker Ltd. All acids were initially recrystallised but as the same product was obtained with or without recrystallisation, they were not subsequently purified.

Metal chlorides : Titanium tetrachloride and aluminium chloride were supplied by Aldrich Chemical Company, Inc., were used without further purification, and were stored in a nitrogen filled dry box. Anhydrous $MgCl_2$ was obtained pure from I.C.I. PLC.

Elemental Analysis

Carbon and hydrogen analyses were carried out by Butterworth Laboratories Ltd, Teddington, and Medac Ltd, Brunel University.

Titanium content was analysed by measuring the absorbance of titanium(IV) peroxo-species at 410nm in acid solution. At concentrations of 10-100ppm the solutions obey the Beer-Lambert laws.

Sample Analysis for Titanium

The test sample (0.01-0.1g) was hydrolysed using concentrated H_2SO_4 ($8cm^3$). The volume of the solution was made up to $90cm^3$ with distilled water and 4 drops of 100 volume H_2O_2 were added. After cooling, the yellow solution was made up to $100cm^3$. The absorbance of the resulting solution was measured with a Pye Unicam SP6-250 spectrometer in a 1cm curvette and compared to the pre-determined calibration graph.

IR Spectra

All IR spectra were recorded using a Perkin-Elmer 580B IR spectrometer and a Perkin Elmer 1720X fourier transform IR spectrometer. Both nujol and hexachlorobutadiene mulls were carried out for each sample between CsI plates. The IR spectra assignments reported are those from the nujol spectra.

NMR Spectra

NMR spectra were recorded on a Brucker Associates ACF 250MHz fourier transform spectrometer.

Crystal Mounting

Crystal mounting was carried out in either of the following ways depending on the air sensitivity of the compound. 0.5mm or 1mm Lindemann tubes were used.

a) Crystals were encased under sodium dried nujol and were mounted into Lindemanns and sealed under an argon atmosphere.

b) Crystals under the solvent were mounted in a nitrogen filled dry box into Lindemanns and sealed with wax. The glass capillary was then sealed by heating when removed from the box.

Preparation of $[Ti_2Cl_7(O_2CR)(RCO_2H)]$ species (R=Et, CMe_3)

Both compounds were prepared by the same method. A typical procedure (for $R=CMe_3$) is as follows.

$TiCl_4$ (1.1cm^3, 10mmol) was added dropwise using a syringe to a stirred solution of trimethylacetic acid (1g, 9.8mmol) in light petroleum ether (40cm^3) in a Schlenk tube at room temperature, under nitrogen. The resulting yellow solution was magnetically stirred for 2 hours, within which time a lemon-yellow precipitate was produced. The reaction liquor solid was removed from the solid using a transfer needle. The solid was then washed with petroleum ether (3x20cm^3) and dried by pumping under vacuum for 6 hours. Yield, 2.31g (86%). (Found : C, 22.22; H, 3.66; Ti, 17.77. $C_{10}H_{19}Cl_7O_4Ti_2$ requires C, 21.99; H, 3.51; Ti, 17.54%). The 250MHz ^1H NMR spectrum ($CDCl_3$) showed resonances at δ10.30(brs) and 1.49-1.13(m). IR bands (cm^{-1}) occur at 3285[υ(OH)](w-m), 1603[$\upsilon(C=O)_{coord.acid}$](s), 1500[$\upsilon(COO)_{asym}$](s), 1485(sh), 1461(s), 1445(sh), 1410(m), 1375(s), 1365[$\upsilon(COO)_{sym}$](s), 1354(m), 1225(s), 1180(m), 1038(m), 872(m), 783(m), 656(m), 615(m), 598(m), 576(m), 560(m), 470(m), 430(s)*, 410(s)*, 370(s)*, 272(m)†.

* Assigned to $\upsilon(Ti\text{-}Cl)_{terminal}$, † assigned to $\upsilon(Ti\text{-}Cl)_{bridging}$.

R=Et

Yield, 89%. (Found : C, 14.82; H, 2.30; Ti, 19.38. $C_6H_{11}Cl_7O_4Ti_2$ requires C, 14.67; H, 2.26; Ti, 19.51%). The 250MHz ^1H NMR spectrum ($CDCl_3$) showed

resonances at δ9.81(brs), 2.88-2.68(m) and 1.40-1.27(m). IR bands (cm^{-1}) occur at 3276[υ(OH)](w-m), 1601[$\upsilon(C{=}O)_{coord.acid}$](s), 1496[$\upsilon(COO)_{asym}$](s), 1463(s), 1419(s), 1374(s), 1365[$\upsilon(COO)_{sym}$](sh), 1303(m), 1180(m), 1084(m), 1020(m), 803(m), 673(m), 579(m), 515(w), 432(s)*, 415(sh)*, 369(m)*, 273(m)†.

* Assigned to $\upsilon(Ti\text{-}Cl)_{terminal}$, † assigned to $\upsilon(Ti\text{-}Cl)_{bridging}$.

Preparation of $[\{TiCl_2(O_2CMe)(MeCO_2H)\}_2O]$

$TiCl_4$ (1.1cm^3, 10mmol) was added dropwise to a stirred solution of acetic acid (1.09cm^3, 25mmol) in toluene (40cm^3) at room temperature. From the resulting red solution a yellow precipitate formed within one minute. The yellow solid was isolated from the reaction liquor by filtration, washed with light petroleum (3x20cm^3) and dried by pumping under vacuum for 5 hours. Yield, 2.15g (87%). (Found : C, 18.93; H, 2.98; Ti, 19.20. $C_8H_{14}Cl_4O_9Ti_2$ requires C, 19.54; H, 2.87; Ti, 19.49%). The 250MHz ^1H NMR spectrum (CD_3CN) showed resonances at δ8.8(brs), and 2.20-1.93(m) (acetate protons overlap with residual protons of CD_3CN). IR bands (cm^{-1}) occur at 3200[υ(OH)](m,br), 1655[$\upsilon(C{=}O)_{coord.acid}$](s), 1540[$\upsilon(COO)_{asym}$](s), 1456(s), 1430[$\upsilon(COO)_{sym}$](s), 1380(s), 1370(sh), 1244(m), 1045(m), 1027(m), 733[υ(TiOTi)](s,br), 650(m), 600(m), 560(m), 485(m), 430(sh)*, 410(s)*, 380(s)*, 350(m)*.

* Assigned to $\upsilon(Ti\text{-}Cl)_{terminal}$

Preparation of $[\{TiCl_2(O_2CEt)(EtCO_2H)\}_2O]$

$TiCl_4$ (1.1cm^3, 10mmol) was added dropwise to a stirred solution of propanoic acid (1.9cm^3, 25mmol) in carbon tetrachloride (40cm^3) at room temperature. The resulting yellow solution was stirred for 4 hours, within which time a colourless precipitate was produced. The solid was isolated from the reaction liquor by filtration and recrystallised from dichloromethane layered with light petroleum. The colourless crystalline product was filtered and washed with light petroleum (2x20cm^3) and dried by pumping under vacuum for

5 hours. Yield (recrystallised product), 2.31g (84%). (Found : C, 26.48; H, 4.22; Ti, 17.50. $C_{12}H_{22}Cl_4O_9Ti_2$ requires C, 26.30; H, 4.05; Ti, 17.48%). The 250MHz ^1H NMR spectrum ($CDCl_3$) showed resonances at δ11.3(brs), 2.65-2.47(m) and 1.36-1.20(m). IR bands (cm^{-1}) occur at 3200[υ(OH)](m,br), 1650[$\upsilon(C=O)_{coord.acid}$](s), 1520[$\upsilon(COO)_{asym}$](s), 1466(s), 1435(sh), 1405[$\upsilon(COO)_{sym}$)](s), 1380(s), 1305(s), 1269(s), 1243(m), 1082(m), 1021(m), 811(m), 736[υ(TiOTi)](s,br), 659(m), 580(m), 488(m), 430(sh)*, 415(s)*, 370(s)*.

* Assigned as $\upsilon(Ti\text{-}Cl)_{terminal}$

Preparation of $[\{TiCl_2(O_2CCMe_3)(Me_3CCO_2H)\}_2O]$

$TiCl_4$ (1.1cm^3, 10mmol) was added dropwise to a stirred solution of trimethylacetic acid (2.55g, 25mmol) in light petroleum ether (40cm^3) at room temperature. The resulting yellow solution was stirred for 5 hours, within which a precipitate was produced. The solid was isolated from the reaction liquor by filtration and recrystallised from dichloromethane layered with petroleum ether. The resulting colourless crystals were washed with light petroleum (3x20cm^3) and dried by pumping under vacuum for 5 hours. Yield (recrystallised product), 2.29g (69%). (Found : C, 36.38; H, 6.04; Ti, 14.30. $C_{20}H_{38}Cl_4O_9Ti_2$ requires C, 36.39; H, 5.80; Ti, 14.51%). The 250MHz ^1H NMR spectrum ($CDCl_3$) showed resonances at δ11.3 (rel.int.1H, brs) and 1.37-1.20 (18H, m). The ^{13}C NMR spectrum ($CDCl_3$) showed resonances at δ26, 27, 39, 40, and 189.5. IR bands (cm^{-1}) occur at 3200[υ(OH)](m,br), 1650[$\upsilon(C=O)_{coord.acid}$](s), 1525[$\upsilon(COO)_{asym}$](s), 1485(s), 1461(s), 1418[$\upsilon(COO)_{sym}$](s), 1378(s), 1281(m), 1224(s), 1205(sh), 1036(m), 875(m), 733[υ(TiOTi)](s,br), 611(m), 540(m), 451(s)*, 405(s)*, 390(s)*, 375(s)*, 335(w).

* Assigned as $\upsilon(Ti\text{-}Cl)_{terminal}$

Preparation of $[Ti_2OCl_3(O_2CEt)_3(EtCO_2H)]$

$TiCl_4$ (1.1cm^3, 10mmol) was added dropwise to a stirred solution of propanoic acid (1.9cm^3, 25mmol) in light petroleum ether (b.p. 60-80°C) and the resulting yellow solution

and precipitate were stirred for 2 days at ambient temperature. The solid was isolated from the reaction liquor by filtration, washed with light petroleum ($3x30cm^3$) and dried by pumping under vacuum for 4 hours. Yield, 2.11g (83%). (Found : C, 27.98; H, 4.09; Ti, 18.52. $C_{12}H_{21}Cl_3O_9Ti_2$ requires C, 28.18; H, 4.14; Ti, 18.73%). The 250MHz ^1H NMR spectrum ($CDCl_3$) showed resonances at δ8.45(brs), 2.70-2.45(m) and 1.35-1.1(m). IR bands (cm^{-1}) occur at 1608 [$\upsilon(C=O)_{coord.acid}$](s), 1520 [$\upsilon(COO)_{asym}$](s), 1456(s), 1397 [$\upsilon(COO)_{sym}$](s), 1370(s), 1270(s), 1083(m), 1021(w), 903(m), 807(m), 720(w), 700(sh), 684 [υ(TiOTi)](m), 557(m), 552(s), 446(s)*, 400(s)*, 350(s)*, 330(sh), 270(w).

* Assigned as $\upsilon(Ti\text{-}Cl)_{terminal}$

Preparation of the species [{$TiCl_2(O_2CR)THF\}_2O$] (R=Me, Et, CMe_3)

All compounds were prepared using the same method. A typical procedure (for R=CMe_3) is as follows.

[{$TiCl_2(O_2CCMe_3)(Me_3CCO_2H)\}_2O$] (1g, 1.5mmol) was dissolved in toluene ($30cm^3$) at room temperature, to which THF ($0.24cm^3$, 3mmol) was added with stirring. After 15 minutes, light petroleum ($70cm^3$) was added to precipitate the product. The solid was isolated by filtration, washed with light petroleum ($3x25cm^3$) and dried by pumping under vacuum for 4 hours. Yield, 0.81g (90%). (Found : C, 35.89; H, 5.65; Ti, 15.89. $C_{18}H_{34}Cl_4O_7Ti_2$ requires C, 36.03; H, 5.71; Ti, 15.97%). The 250MHz ^1H NMR spectrum ($CDCl_3$) showed resonances at δ4.8(8H,brs), 2.20(8H,brs) and 1.34-1.25 (18H,m). IR bands (cm^{-1}) occur at 1525[$\upsilon(COO)_{asym}$](s), 1480(sh), 1457(s), 1420[$\upsilon(COO)_{sym}$](s), 1378(s), 1365(sh), 1226(s), 1030(w), 1009[$\upsilon(COC)_{asym}$](m-s), 924(m), 858[$\upsilon(COC)_{sym}$], 780(sh), 724[υ(TiOTi)](s,br), 675(m), 599(m), 550(w), 453(s)*, 390(s)*, 350(s)*.

* Assigned as $\upsilon(Ti\text{-}Cl)_{terminal}$

R=Et

Yield, (79%). (Found : C, 30.56; H, 4.79; Ti, 17.60. $C_{14}H_{26}Cl_4O_7Ti_2$ requires C, 30.93; H, 4.82; Ti, 17.62%). The 250MHz ^1H NMR spectrum ($CDCl_3$) showed resonances at δ4.90(8H,brs), 2.63-2.47(4H,m), 2.22(8H,brs) and 1.27-1.15 (6H,m). IR bands (cm^{-1}) occur at 1531[$\upsilon(COO)_{asym}$](s), 1463(s), 1430[$\upsilon(COO)_{sym}$](s,sh), 1378(s), 1302(m), 1082(w), 1012[$\upsilon(COC)_{asym}$](m), 958(w), 923(w), 855(w-m), 821[$\upsilon(COC)_{sym}$](m), 725[υ(TiOTi)](m-s), 672(m), 600(m), 565(w), 511(w), 430(sh)*, 420(s)*, 400(sh)*, 350(s)*.

* Assigned as $\upsilon(Ti\text{-}Cl)_{terminal}$

R=Me

Yield, (86%). (Found : C, 27.50; H, 4.19; Ti, 18.64. $C_{12}H_{22}Cl_4O_7Ti_2$ requires C, 27.95; H, 4.30; Ti, 18.58%). The 250MHz ^1H NMR spectrum ($CDCl_3$) showed resonances at δ4.80(8H,brs), 2.23(8H,brs) and 2.23-1.85(6H,m). IR bands (cm^{-1}) occur at 1547[$\upsilon(COO)_{asym}$](s), 1457(m), 1447[$\upsilon(COO)_{sym}$](s), 1410(sh), 1379(m), 1253(w), 1177(w), 1041(m), 1010[$\upsilon(COC)_{asym}$](s), 960(m),922(m), 857[$\upsilon(COC)_{sym}$](s), 750(sh), 723[υ(TiOTi)](s), 715(sh), 681(m), 633(w), 553(w), 430(sh)*, 421(s)*,380(s)*, 355(s)*.

* Assigned as $\upsilon(Ti\text{-}Cl)_{terminal}$

Preparation of $[\{TiCl_2(O_2CCH_2OC_6F_5)\}_2O]0.5C_6H_{14}$

$TiCl_4$ ($0.5cm^3$, 4.5mmol) was added dropwise to a stirred solution of pentafluorophenoxyacetic acid (1.65g, 6.8mmol) in benzene ($40cm^3$) at room temperature. After stirring for 15 minutes, the fibrous precipitate was isolated by filtration, washed with hexane ($3x30cm^3$) and dried by pumping under vacuum for 6 hours. Yield, 1.12g (68%). (Found : C, 28.92; H, 1.39; Ti, 12.40. $C_{19}H_{11}Cl_4F_{10}O_7Ti_2$ requires C, 29.30; H, 1.42; Ti , 12.30%). The 250MHz ^1H NMR spectrum (d^8-toluene) shows resonances at δ5.23(1H,d,J=15Hz) and 4.98(1H,d,J=15Hz). Solvent resonances ($[\{TiCl_2(O_2CCH_2OC_6F_5)\}_2O]$: C_6H_{14}. 1: 0.5) also present. IR bands (cm^{-1}) occur at

1626[$\upsilon(COO)_{asym}$](s), 1587[$\upsilon(COO)_{asym}$](s), 1523(s), 1460(s), 1450[$\upsilon(COO)_{sym}$](s), 1415(s), 1379(m), 1343(m), 1313(m), 1222(w), 1155(w), 1067(w-m), 1038[$\upsilon(COC)_{asym}$](s), 1004(s), 977(s), 760(w), 735[υ(TiOTi)](m-s), 684(m), 643(s), 578(m), 531(s), 448(s)*, 421(s)*, 385(s)*, 345(m)*.

* Assigned to $\upsilon(Ti\text{-}Cl)_{terminal}$.

Preparation of [{$TiCl_2(O_2CCH_2OC_6F_5)THF\}_2O$]

$TiCl_4$ (0.5cm^3, 4.5mmol) was added dropwise to a stirred solution of pentafluorophenoxyacetic acid (1.65g, 6.8mmol) in benzene (40cm^3) at room temperature. To this mixture THF (0.36cm^3, 4.5mmol) was added in a dropwise fashion, and the reaction solution was stirred for 30 minutes. The titled product was precipitated from the solution by addition of light petroleum (100cm^3) and the yellow powder was isolated by filtration, washed with petroleum ether (3x30cm^3) and dried by pumping under vacuum for 4 hours. Yield, 1.71g (86%). (Found C, 32.45; H, 2.34; Ti, 10.90. $C_{24}H_{20}Cl_4F_{10}O_7Ti_2$ requires C, 32.77; H, 2.29; Ti, 10.89%). The ^{1}H NMR spectrum shows resonances at δ4.86(4H,brs), 4.62-4.40(8H,brm) and 2.15-2.05(8H,brm). IR bands (cm^{-1}) occur at 1595[$\upsilon(COO)_{asym}$](s), 1517(s), 1460(s), 1450[$\upsilon(COO)_{sym}$](sh), 1424(m), 1379(m), 1336(m), 1305(m), 1254(w), 1160(m), 1058(s), 1037(m), 1000(s) 990[$\upsilon(COC)_{asym}$](sh), 955(m), 837[$\upsilon(COC)_{sym}$](m), 748[υ(TiOTi)](m), 721(m), 681(w), 616(w), 565(w), 509(w), 509(w), 430(s)*, 415(s)*, 380(s)*, 330(w)*.

* Assigned to $\upsilon(Ti\text{-}Cl)_{terminal}$.

Preparation of [{$TiOCl(O_2CCMe_3)THF\}_4$]

[{$TiCl_2(O_2CCMe_3)(Me_3CCO_2H)\}_2O$] (2g, 3mmol) was dissolved in toluene (40cm^3) at room temperature. To this solution a mixture of distilled water (54μl, 3mmol) in THF (0.48cm^3, 6mmol) was added dropwise. The solution subsequently turned from yellow to colourless. The solution was stirred for a further 15 minutes after which time light petroleum (150cm^3) was layered onto the solution to precipitate the colourless crystalline

product. The solid was isolated by filtration, washed with light petroleum (3x25cm^3) and dried by pumping under vacuum for 4 hours. Yield, 1.33g (81%). (Found : C, 39.81; H, 6.20; Ti, 17.98. $C_{36}H_{68}Cl_4O_{16}Ti_4$ requires C, 39.67; H, 6.29; Ti, 17.58%). The 250MHz ^{1}H NMR spectrum ($CDCl_3$) shows resonances at δ3.96(16H,brs), 1.90(16H, brs) and 1.38-1.11(36H,m). IR bands (cm^{-1}) occur at 1575[$\upsilon(COO)_{asym}$](s), 1480(m), 1461(s), 1430[$\upsilon(COO)_{sym}$](m), 1378(s), 1360(sh), 1231(m), 1026[$\upsilon(COC)_{asym}$](m), 881[$\upsilon(COC)_{sym}$](m), 805(sh), 791[υ(TiOTi)](s), 770(sh), 608(m), 455(m), 425(w), 375[$\upsilon(TiCl)_{terminal}$](m), 345(w), 330(w).

Preparation of $[Ti_3O_2Cl_3(O_2CEt)_5]$

$[\{TiCl_2(O_2CEt)(EtCO_2H)\}_2O]$ (1g, 1.8mmol) was suspended in light petroleum (b.p.60-80°C, 30cm^3) and refluxed for 30 minutes to give a white precipitate. After cooling, the precipitate was isolated from the reaction liquor by filtration and recrystallised from a dichloromethane solution (20cm^3) layered with light petroleum (70cm^3). The colourless crystals were filtered, washed with cold petroleum (3x20cm^3) and dried by pumping under vacuum for 4 hours. Yield, 0.66g (85%). (Found : C, 27.47; H, 3.95; Ti, 22.09. $C_{15}H_{25}Cl_3O_{12}Ti_3$ requires C, 27.84; H, 3.89; Ti, 22.21%). The ^{1}H NMR spectrum ($CDCl_3$) 250MHz showed resonances at δ2.62-2.45 (2H,m) and 1.33-1.11(3H,m). Major IR bands (cm^{-1}) occur at 1561[$\upsilon(COO)_{asym}$](s), 1530[$\upsilon(COO)_{asym}$)](s), 1466(s), 1440[$\upsilon(COO)_{sym}$](s), 1407[$\upsilon(COO)_{sym}$](s), 1378(s), 1280(s), 1086(m), 1081(m), 901(w), 812(m), 715(m), 680(m), 645(s), 597(m), 570(m), 450(m)*, 420(m), 365(m,sh), 340(s)*.

* Assigned to $\upsilon(Ti\text{-}Cl)_{terminal}$.

Preparation of $[Ti_3O_2Cl_3(O_2CCMe_3)_5]$

$[\{TiCl_2(O_2CCMe_3)(Me_3CCO_2H)\}_2O]$ (1.5g, 2.3mmol) was suspended in light petroleum (b.p.60-80°C, 40cm^3) and heated to 40°C for 30 minutes within which time the precipitate dissolved. Some solvent was then removed to precipitate the product and the

colourless powder was isolated by filtration, washed with cold, light petroleum (3x20cm^3) and dried by pumping under vacuum for 4 hours. Yield, 0.96g (80%). (Found : C, 39.62; H, 6.02; Ti, 18.77. $C_{25}H_{45}Cl_3O_{12}Ti_3$ requires C, 38.12; H, 5.72; Ti, 18.26%). The ^{1}H NMR spectrum ($CDCl_3$) 250MHz showed resonances at δ1.28(18H,s), 1.25(18H,s) and 1.20(9H,s). Major IR bands (cm^{-1}) occur at 1558[$\upsilon(COO)_{asym}$](s), 1522[$\upsilon(COO)_{asym}$)](s), 1462(s), 1427[$\upsilon(COO)_{sym}$](s), 1410[$\upsilon(COO)_{sym}$](s), 1380(s), 1224(s), 1034(w), 785(m), 716(m), 665[υ(TiOTi)](s), 611(s),558(m), 475(s), 408(m), 375(sh), 355(s)*.

* Assigned to $\upsilon(Ti\text{-}Cl)_{terminal}$.

Preparation of [{TiCl(O$_2$CCMe$_3$)$_2$}$_2$O]

$TiCl_4$ (1.1cm^3, 10mmol) was added dropwise to a stirred solution of pivaloyl anhydride (6.5cm^3, 25mmol) in petroleum ether (b.p. 100-120°C) at room temperature. The reaction solution was then heated to reflux for 3 hours upon which time a colourless precipitate was produced. The solid was isolated from the reaction mixture by filtration, washed with light petroleum (b.p. 60-80°C, 3x25cm^3) and dried by pumping under vacuum for 5 hours. Yield, 2.61g (88%). (Found : C, 41.19; H, 6.13; Ti, 16.02. $C_{20}H_{36}Cl_2O_9Ti_2$ requires C, 40.90; H, 6.18; Ti, 16.31%). Sample was too insoluble for NMR experiments. Major IR bands (cm^{-1}) occur at 1590[$\upsilon(COO)_{asym}$](s), 1550[$\upsilon(COO)_{asym}$)](s), 1510[$\upsilon(COO)_{sym}$](s), 1485(sh), 1461(s), 1413[$\upsilon(COO)_{sym}$](s), 1378(s), 1225(s), 1034(w), 939(w), 778(m), 720[υ(TiOTi)](s,br), 603(s), 560(s), 461(s), 410(m)*, 390(m)*, 375(m)*, 335(m)*.

* Assigned to $\upsilon(Ti\text{-}Cl)_{terminal}$.

Preparation of [{Ti$_3$O$_2$Cl(OEt)$_3$(O$_2$CCH$_2$C$_6$F$_5$)$_4$}$_2$]

$TiCl_4$ (0.2cm^3, 1.8mmol) was added dropwise to a stirred solution of pentafluorophenylacetic acid (0.81g, 3.6mmol) in chloroform* (40cm^3) at room temperature. The solution became a clear pale yellow and was stirred for a further two

hours. Chloroform ($30cm^3$) was then removed by vacuum, and light petroleum ($40cm^3$) was added to precipitate a white solid which was isolated by filtration and washed with light petroleum ($1x20cm^3$). The solid was left in light petroleum ($20cm^3$) for 3 days within which time crystals were produced. The crystals were mounted in Lindemann tubes under argon for X-ray structural determination. IR bands (cm^{-1}) occur at 1659(m), 1600[$\upsilon(COO)_{asym}$](m), 1572[$\upsilon(COO)_{sym}$](s), 1524(s), 1505(s), 1459(m), 1434[$\upsilon(COO)_{sym}$](s), 1395[$\upsilon(COO)_{sym}$](s), 1378(s), 1321(m), 1272(w), 1202(w), 1127(m), 1115[$\upsilon(CO)_{terminal}$](m,sh), 1074[$\upsilon(CO)_{bridging}$](m), 1014(s), 986(m), 938(w), 915(m), 814(m), 776(w), 707(w), 691(w), 660(m), 643(m), 618(sh), 531(m), 471(m).

* Chloroform stabilised with ethanol

Preparation of $[\{TiCl_2(O_2CC_6F_5)(C_6F_5CO_2H)\}_2O]$

$TiCl_4$ ($0.35cm^3$, 3.1mmol) was added dropwise to a stirred solution of pentafluorobenzoic acid (1.67g, 7.75mmol) in toluene ($40cm^3$) at room temperature. The resultant solution was stirred for 3 hours and then light petroleum ($120cm^3$) was added to precipitate a pale yellow solid. The product was isolated by filtration, washed with light petroleum ($3x25cm^3$) and dried by pumping under vacuum for 5 hours. Yield, 1.42g (84%). (Found : C, 30.69; Ti, 9.01. $C_{28}H_2Cl_4F_{20}O_9Ti_2$ requires C, 30.58; Ti, 8.71%). IR bands (cm^{-1}) occur at 1651(s), 1613[$\upsilon(C=O)_{coord.acid}$](s), 1543[$\upsilon(COO)_{asym}$](s), 1527(s), 1489(s), 1465(s), 1390[$\upsilon(COO)_{sym}$](s,sh), 1380(s), 1301(s), 1156(m) 1135(m), 1125(m), 1008(s), 956(s), 813(s), 780(w), 752[$\upsilon(TiOTi)$](m-s), 713(w), 659(w), 587(w), 512(m), 493(s), 461(m), 426(m)*, 398(m)*,362(m)*, 322(w), 300(m).

* Assigned to $\upsilon(Ti\text{-}Cl)_{terminal}$.

Preparation of $[\{TiCl_2(O_2CCH_2C_6F_5)(C_6F_5CH_2CO_2H)\}_2O]$ Form A

$TiCl_4$ ($0.39cm^3$, 3.5mmol) was added dropwise to a stirred solution of pentafluorophenylacetic acid (1.98g, 8.75mmol) in carbon tetrachloride ($40cm^3$) at room temperature. The resulting yellow solution was stirred for 3 hours and then light petroleum

($100cm^3$) was added to precipitate a yellow solid. The solid was isolated by filtration, washed with a carbon tetrachloride / light petroleum (20:80) solution ($3x20cm^3$) and dried by pumping under vacuum for 8 hours. Yield, 1.65g (82%). (Found : C, 33.71; H, 0.97; Ti, 8.15. $C_{32}H_{10}Cl_4F_{20}O_9Ti_2$ requires C, 33.26; H, 0.87; Ti, 8.29%). The 250MHz ^1H NMR spectrum ($CDCl_3$) shows resonances at δ9.02 (brs), 3.98 (2H,s), 3.97(2H,s), 3.93(10H,s) and 3.80(2H,s). IR bands (cm^{-1}) occur at 1661(m), 1632[$\upsilon(C=O)_{coord.acid}$](m), 1545[$\upsilon(COO)_{asym}$](s), 1525(s), 1509(s), 1462(s), 1415(m-s), 1385[$\upsilon(COO)_{sym}$](s,sh), 1375(s), 1322(m), 1270(m), 1130(m), 1017(s), 987(m), 951(w), 917(m), 787[υ(TiOTi)](m), 737(w), 711(w), 657(m), 565(w), 497(m), 457(m), 420(m)*, 384(m)*, 362(m)*.

* Assigned to $\upsilon(Ti\text{-}Cl)_{terminal}$.

Preparation of $[\{TiCl_2(O_2CCH_2C_6F_5)(C_6F_5CH_2CO_2H)\}_2O]$ Form B

$TiCl_4$ ($0.4cm^3$, 3.5mmol) was added dropwise to a stirred solution of pentafluorophenylacetic acid (2g, 8.9mmol) in chloroform ($40cm^3$) at room temperature. The resulting yellow solution was stirred for 3 hours and then carefully layered with light petroleum ($120cm^3$). The reaction mixture was left undisturbed for one week at room temperature whereupon diffusion of solvents led to a cream precipitate. The product was isolated by filtration, washed with light petroleum ($3x20cm^3$) and dried by pumping under vacuum for 3 hours. Yield, 1.41g (70%). (Found : C, 33.91; H, 0,90; Ti, 8.45. $C_{32}H_{10}Cl_4F_{20}O_9Ti_2$ requires C, 33.26; H, 0.87; Ti, 8.29%). The 250MHz ^1H NMR spectrum ($CDCl_3$) shows resonances at δ9.51(brs), 3.98(2H,s), 3.97(2H,s), 3.93(10H,s) and 3.80(2H,s). IR bands (cm^{-1}) occur at 1687[$\upsilon(COO)_{asym}$](s), 1659(m), 1606[$\upsilon(C=O)_{coord.acid}$](m), 1548[$\upsilon(COO)_{asym}$](s), 1524(s), 1508(s), 1463(s), 1433(s), 1395[$\upsilon(COO)_{sym}$](s,sh), 1390[$\upsilon(COO)_{sym}$](s,sh), 1385(s), 1327(s), 1273(m), 1224(m), 1210(m), 1130(s), 1016(s), 992(m), 914(m), 781(m), 740[υ(TiOTi)](s), 711(m), 657(m), 618(w), 568(w), 534(w), 499(m), 456(s)*, 385(s)*, 330(m), 280(s,br)†

* Assigned to $\upsilon(Ti\text{-}Cl)_{terminal}$, † assigned to $\upsilon(Ti\text{-}Cl)_{bridging}$

Preparation of $[\{TiO(O_2CC_6F_5)_2\}_8.3C_6H_5CH_3]$

$TiCl_4$ (0.35cm^3, 3.1mmol) was added dropwise to a stirred solution of pentafluorobenzoic acid (1.97g, 9.3mmol) in toluene (40cm^3) at ambient temperature. The resulting orange solution was heated to reflux for 3 hours and then allowed to cool. Light petroleum (150cm^3) was then carefully layered on top of the resultant solution which was allowed to stand at room temperature for 2 weeks within which time a golden crystalline product was formed. The product was isolated by filtration, washed with a toluene / light petroleum (10:90) mixture (4x20cm^3) and dried by pumping under vacuum for 12 hours. Yield, 1.21g (80%). (Found : C, 38.65; H, 0.60; Ti, 9.09. $C_{133}H_{24}F_{80}O_{40}Ti_8$ requires C, 38.37; H, 0.58; Ti, 9.20%). IR bands (cm^{-1}) occur at 1651(m), 1576[$\upsilon(COO)_{asym}$](s), 1526(m), 1494(m), 1464(m), 1400[$\upsilon(COO)_{sym}$](s,br), 1301(m), 1125(m), 1029(s), 945(m), 769[υ(TiOTi)](s,br), 735(s), 611(w), 587(w), 536(m), 476(m), 444(m).

Preparation of $[\{TiO(O_2CCH_2C_6F_5)_2\}_8.]$

$TiCl_4$ (0.39cm^3, 3.5mmol) was added dropwise to a stirred solution of pentafluorophenylacetic acid (2.4g, 10.6mmol) in toluene (40cm^3) at room temperature. The resulting yellow-orange solution was heated to reflux for 5 hours and then some toluene (30cm^3) was removed. Light petroleum (150cm^3) was added to the stirred solution and the mixture was placed in a freezer (-25°C) for 1 week whereupon after a while a crystalline precipitate had deposited. The solid was isolated by filtration, washed with cold, light petroleum (3x20cm^3) and dried by pumping under vacuum for 5 hours. Yield, 0.90g (50%). (Found : C, 37.51; H, 0.83; Ti, 9.10. $C_{128}H_{32}F_{80}O_{40}Ti_8$ requires C, 37.39; H, 0.78; Ti, 9.32%). The 250MHz ^{1}H NMR spectrum ($CDCl_3$) showed resonances at δ3.81(2H,s) and 3.40(2H,s). IR bands (cm^{-1}) occur at 1661(m), 1572[$\upsilon(COO)_{asym}$](s), 1525(s), 1507(s), 1460(s), 1420(s), 1398[$\upsilon(COO)_{sym}$](s), 1380(s), 1320(m), 1271(w), 1201(w), 1127(m), 1018(s), 981(m), 917(m), 782[υ(TiOTi)](m), 757(m), 730(w,sh), 660(m), 567(w), 527(w), 462(w), 411(w).

Preparation of $[Ti_3O_2Cl_4(O_2CCH_2OC_6F_5)_4].0.75C_6H_6.0.25C_6H_{14}$

$TiCl_4$ (0.22cm^3, 2mmol) was added dropwise to a stirred solution of pentafluorophenoxyacetic acid (0.97g, 4mmol) in benzene (40cm^3) at room temperature. The resulting yellow-orange solution was heated to reflux for 5 hours and allowed to cool. Light petroleum (150cm^3) was then carefully layered on top of the reaction solution which was allowed to stand for 2 weeks at room temperature after which time a golden yellow crystalline product had formed. The product was isolated by filtration, washed with hexane (3x30cm^3) and dried by pumping under vacuum for 6 hours. Yield, 0.44g, (49%). (Found : C, 33.71; H, 1.21; Ti, 10.72. $C_{38}H_{16}Cl_4F_{20}O_{14}Ti_3$ requires C, 33.52; H, 1.18; Ti, 10.55%). The 250MHz ^1H NMR spectrum (d^8-toluene) showed one resonance at δ4.30. Sovent resonances ($[Ti_3O_2Cl_4(O_2CCH_2OC_6F_5)_4] : C_6H_6 : C_6H_{14}$ 1:0.75:0.25 also present. IR bands (cm^{-1}) occur at 1584[$\upsilon(COO)_{asym}$](s,br), 1560[$\upsilon(COO)_{asym}$](s), 1518(s), 1460(s), 1450[$\upsilon(COO)_{sym}$](sh), 1410[$\upsilon(COO)_{sym}$](s), 1380(m), 1340(m), 1302(m), 1165(m), 1069(s), 1037(m), 993(s), 958(m), 824(m), 736(m), 718[υ(TiOTi)](m), 683(m), 639(m), 576(m), 526(m), 440(sh,m)*, 430(m)*, 415(m)*, 390(m)*.

* Assigned to $\upsilon(Ti\text{-}Cl)_{terminal}$

HANDLING TECHNIQUES

The compounds were handled under nitrogen in Schlenk tubes fitted with Suba seals (or stoppers) attached to a conventional Schlenk line. Solvents were added, or removed from other Schlenk tubes using 18 gauge transfer needles, and TiCl4 and the acids (in solution if necessary) were added from luer-lock syringes fitted with appropriate needles. When Schlenk tubes were left to stand or put in the freezer, they were protected by Parafilm. Compounds were also handled in a nitrogen filled Miller Howe glove box. The atmosphere was controlled by circulating the gas through two columns one containing molecular sieve (type 4A), and the other copper on a ceramic support which removed water and oxygen

respectively down to less than 5 p.p.m. All items introduced into the box were carefully dried prior to placing them in the port. The port was evacuated at least three times before opening to the box. Good quality gloves made from butyl rubber were used to limit contamination of the glove box atmosphere.

Solution Catalysis Experiments for the Polymerisation of Propene

The investigations were carried out in an analogous fashion. Reactant quantities may be found in Table 8.1. A typical experiment is given for $[\{TiCl_2(O_2CCH_2OC_6F_5)\}_2O]$ with $AlEt_3$ activator.

Polymerisation of Propene using $[\{TiCl_2(O_2CCH_2OC_6F_5)\}_2O]$

$[\{TiCl_2(O_2CCH_2OC_6F_5)\}_2O]$ (0.267g, 0.36mmol) was dissolved in dry toluene ($30cm^3$) in a Schlenk tube. Propene gas was then added for 10 minutes to allow both the solution and the Schlenk atmosphere to become saturated. The activator, $AlEt_3$ ($2cm^3$, 2mmol) was then added by syringe and the solution was stirred under a propene atmosphere at room temperature for 1 hour.

The reaction product was then poured into methanol ($200cm^3$), to which H_2SO_4 ($100cm^3$, 2.5M) was added. The mixture was then filtered and the residue was washed with methanol and dried at 50°C for 1 day. Yield of polymer = 0.04g.

Compound	Molecular weight	Compound weight (g)	N° mole Ti (mmol)	Activator	Concentration	Amount of activator used (cm^3)	Al:Ti ratio	Polymer yield (g)	Polymer yield (g/mmol Ti)
$[\{TiCl_2(O_2CCH_2OC_6F_5)\}_2O]$	735.6	0.267	0.73	$AlEt_3$	1M	2	3:1	0.04	0.05
$[\{TiCl_2(O_2CEt)(EtCO_2H)\}_2O]$	547.6	0.245	0.89	$AlEt_3$	1M	12	13:1	nil	-
$[\{TiCl_2(O_2CC_6F_5)(C_6F_5CO_2H)\}_2O]$	1099.6	0.454	0.83	$AlEt_3$	1M	10	12:1	0.10	0.12
$[\{TiOCl(O_2CCMe_3)THF\}_4]$	1089.8	0.076	0.28	$AlEt_3$	1M	10	36:1	nil	-

Table 8.1 Solution catalysis results and experimental conditions

Heterogeneous Catalysis Experiments for the Polymerisation of Propene

The investigations were carried out in an analogous fashion. Reactant quantities may be found in Table 8.2. A typical experiment is given for $[Ti_2Cl_7(O_2CEt)(EtCO_2H)]$ with $AlEt_3$ activator. The magnesium chloride utilised was subjected to sonic vibrations for 2 days to reduce the particle size.

Polymerisation of Propene using $[Ti_2Cl_7(O_2CEt)(EtCO_2H)]$

Magnesium chloride (0.924g, 9.7mmol) was placed in a Schlenk tube along with $[Ti_2Cl_7(O_2CEt)(EtCO_2H)]$ (0.127g, 0.26mmol). The mixture was stirred in toluene ($30cm^3$) for 3 hours then allowed to settle. The supernatant was syringed off and the solid was washed with EC180 ($1x20cm^3$) before resuspending in EC180 ($30cm^3$). Propene gas was then added for 10 minutes to allow both the solution and the Schlenk atmosphere to become saturated. Triethylaluminium ($10cm^3$, 10mmol) was then added by syringe and the solution was stirred under a propene atmosphere at room temperature for 1 hour.

The reaction liquor was syringed off and H_2SO_4 ($50cm^3$) was then carefully added to dissolve any alumina. The organic layer was then added to acetone ($200cm^3$) and the precipitate was filtered and dried at 50°C for 1 day. Yield of polymer = 1.75g.

Compound	Molecular weight	Compound weight (g)	Amount of $MgCl_2$ (g)	Activator	Concentration	Amount of activator used (cm^3)	Polymer yield (g)	Polymer yield (g/g $MgCl_2$)
$[\{TiCl_2(O_2CCH_2OC_6F_5)\}_2O]$	735.6	0.097	0.752	$AlEt_3$	1M	10	0.097	0.12
$[\{Ti_2Cl_7(O_2CEt)(EtCO_2H)]$	491.0	0.127	0.924	$AlEt_3$	1M	10	1.750	1.89
$[\{TiCl_2(O_2CC_6F_5)(C_6F_5CO_2H)\}_2O]$	1099.6	0.287	0.875	$AlEt_3$	1M	10	0.934	1.07
$[\{Ti_2OCl_3(O_2CEt)_3(EtCO_2H)]$	511.2	0.119	0.611	$AlEt_3$	1M	10	0.128	0.21
$[\{TiOCl(O_2CCMe_3)THF\}_4]$	1089.8	0.054	0.611	$AlEt_3$	1M	10	nil	-

Table 8.2 Heterogeneous catalysis results and experimental conditions

Preparation of $[AlCl_2(O_2CR)]$ (R=Et, CMe_3)

Both compounds were prepared by the same method. A typical procedure (for R=CMe_3) is as follows.

Trimethylacetic acid (0.84g, 8.2mmol) in chloroform ($30cm^3$) was added to a suspension of $AlCl_3$ (1.06g, 8.0mmol) also in chlororform ($30cm^3$) at room temperature. The solution was then heated to 50°C for 2 hours to give a clear yellow solution. The solution was then filtered to remove any solid residues of $AlCl_3$, and light petroleum ($100cm^3$) was added to the filtrate. The solution was then stored at -10°C for 1 week within which time a crystalline product precipitated. The solid was isolated from the liquors by filtration, washed with light petroleum ($3x25cm^3$) and dried by pumping under vacuum for 4 hours. Yield, 1.15g (72%). (Found : C, 30.53; H, 4.61. $C_5H_9Cl_2O_2Al$ requires C, 30.17; H, 4.56%). The 250MHz ^1H NMR spectrum ($CDCl_3$) shows a singlet at δ1.37. IR bands (cm^{-1}) occur at 1587[$\upsilon(COO)_{asym}$](s,br), 1495(s), 1460[$\upsilon(COO)_{sym}$](s), 1377(s), 1236(s), 1039(w), 942(w), 790(m), 692(m), 607(m), 547(s), 481(m), 431(w).

R=Et

Yield (65%). (Found : C, 20.87; H, 3.10. $C_3H_5Cl_2O_2Al$ requires C, 21.08; H, 2.95%). The 250MHz ^1H NMR spectrum ($CDCl_3$) shows a quartet centred at δ2.86 (2H) and a triplet centred at δ1.33 (3H). IR bands (cm^{-1}) occur at 1575[$\upsilon(COO)_{asym}$](s,br), 1470[$\upsilon(COO)_{sym}$](s), 1456(s), 1401(m), 1382(s), 1317(s), 1267(w), 1090(m), 1032(w), 937(m), 814(s), 751(s), 546(s,br), 494(s), 469(s).

Preparation of $[AlCl(O_2CEt)_2]$

Propanoic acid ($1.37cm^3$, 18mmol) was added to a solution of $AlCl_3$ (1.19g, 9mmol) in toluene ($40cm^3$) at room temperature. The solution was then heated to reflux for 2 hours. When cool, light petroleum was added ($120cm^3$) to precipitate a solid. The product was isolated from the reaction liquors by filtration, washed with cold petroleum ether ($3x25cm^3$) and dried by pumping under vacuum for 5 hours. Yield 1.70g (90%).

(Found : C, 34.27; H, 4.79. $C_6H_{10}ClO_4Al$ requires C, 34.57; H, 4.84). The 250MHz ^1H NMR spectrum ($CDCl_3$) shows resonances at δ2.57(2H,q), 2.37(6H,q), 1.24(3H,t) and 1.08(9H,t). IR bands (cm^{-1}) occur at 1636[$\upsilon(COO)_{asym}$](m), 1604[$\upsilon(COO)_{asym}$](m), 1568[$\upsilon(COO)_{asym}$](s), 1555[$\upsilon(COO)_{asym/sym}$](s,sh), 1480[$\upsilon(COO)_{sym}$](s), 1470[$\upsilon(COO)_{sym}$](s), 1463[$\upsilon(COO)_{sym}$](s), 1408(m), 1379(m), 1314(m), 1277(m), 1085(m), 1024(w), 944(w), 814(m), 722(m), 645(m), 593(w), 539(w), 494(s), 429(w).

Preparation of $[Al(OH)(O_2CPh)_2]$

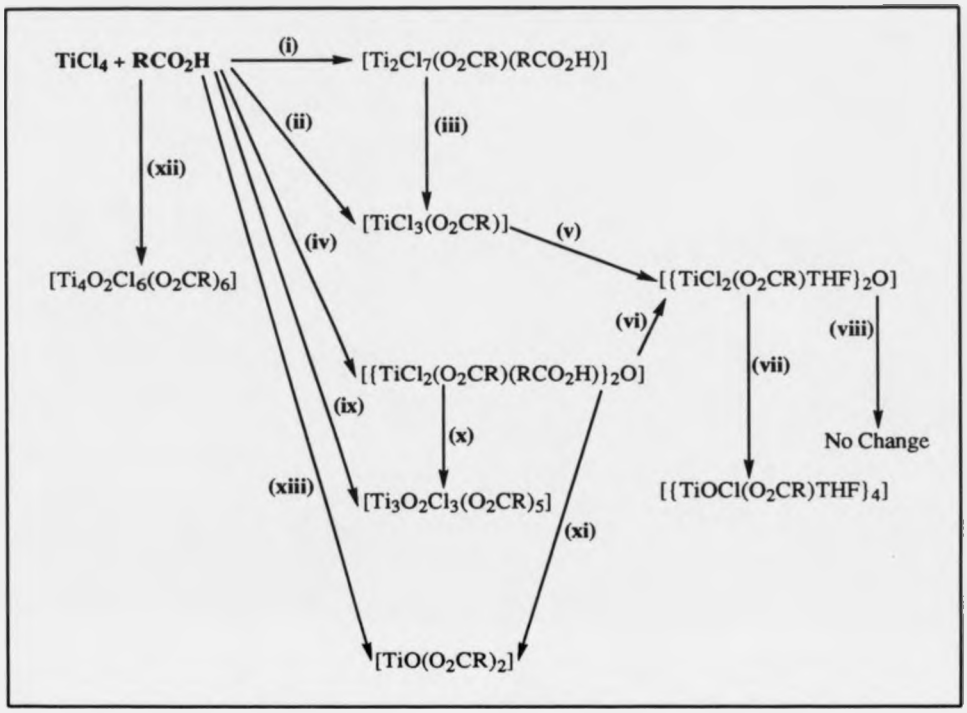
Benzoic acid (1.55g, 12.7mmol) was dissolved in acetonitrile ($30cm^3$) and the solution was added dropwise to a stirred solution of aluminium chloride (0.82g, 6.2mmol) in acetonitrile ($30cm^3$) at room temperature. The solution was then heated to reflux for 2 hours within which time a white precipitate was produced. The solid was isolated from the reaction liquor by filtration, washed with cold acetonitrile ($3x25cm^3$) and dried by pumping under vacuum for 4 hours. Yield, 1.52g (86%). (Found : C, 59.01; H, 3.91. $C_{14}H_{11}O_5Al$ requires C, 58.79; H, 3.88%). Sample was too insoluble for NMR studies to be carried out. IR bands (cm^{-1}) occur at 3676[$\upsilon(OH)$](w), 1610(sh), 1600(s), 1562[$\upsilon(COO)_{asym}$](s), 1495(s), 1440[$\upsilon(COO)_{sym}$](s,br), 1377(s), 1308(w), 1182(w), 1158(w), 1070(w), 1028(w), 989[δ(OH)], 939(w), 852(w), 721(s), 686(m), 606(m), 547(s), 435(m), 380(m), 355(m), 340(m), 320(m).

CONCLUSIONS

We have seen throughout this thesis the preparation of titanium carboxylate species which may subsequently be converted, by heat or hydrolysis, to other titanium(IV) carboxylate compounds. The chemistry of $TiCl_4$ with carboxylic acids has been carried out within these laboratories for 12 years and the findings have proved useful in assessing the overall reaction pathways which can occur. These routes are displayed in Figure 8.1, which serves to show the many different species which have been identified.

No evidence for the adduct $[TiCl_4.RCO_2H]$ has been found, but the intermediates $[Ti_2Cl_7(O_2CR)(RCO_2H)]$ (R=Et, CMe_3) have been prepared in addition to those which have been previously isolated for R=*p*-XC_6H_4, (X=F, Cl, Br) and MeCH=CH.[170] Heating the compound $[Ti_2Cl_7(O_2CC_6H_4Cl\text{-}p)(p\text{-}ClC_6H_4CO_2H)]$ has been found to give $[TiCl_3(O_2CC_6H_4Cl\text{-}p)]$ with the elimination of hydrogen chloride gas,[188] but initial results for this thesis on heating the propanoate and trimethylacetate derivatives have only produced oils, which on analysis, have appeared to be mixtures. However, continuing work by these laboratories has now shown that on suspending these latter two compounds in light petroleum ether (b. p. 60-80°C) with refluxing, the products $[TiCl_3(O_2CEt)]$ and $[TiCl_3(O_2CCMe_3)]$ may be isolated.

In attempting to prepare $[TiCl_2(O_2CR)_2]$ derivatives using a 1:2.5 ratio of $TiCl_4$ to RCO_2H (R=Me, Et, CMe_3, C_6F_5, $CH_2C_6F_5$) at room temperature, the oxo bridged species $[\{TiCl_2(O_2CR)(RCO_2H)\}_2O]$ were formed. These compounds are proposed as forming *via* the production of acid chloride which has been seen in the IR spectrum of the mother liquors for each reaction solution. The co-ordinated acid ligand in these compounds reacts further on heating to eliminate HCl and by a series of further reactions produces $[Ti_3O_2Cl_3(O_2CR)_5]$ (R=Et, CMe_3) and $[\{TiO(O_2CR)_2\}_8]$ (R=C_6F_5, $CH_2C_6F_5$). It should be noted that the acetic acid derivative $[\{TiCl_2(O_2CMe)(MeCO_2H)\}_2O]$ does not appear to react further on refluxing in toluene. It is possible that an increased length of



(i) 1:1, 0-25°C, [R=Et, CMe_3, *p*-XC_6F_4 (X=F, Cl, Br), MeCH=CH]

(ii) 1:1, toluene, 50-70°C, [R=Ph, *o*-MeC_6H_4, *p*-MeC_6H_4, 2,4,6-$Me_3C_6H_2$, $CMePh_2$, $CHMe_2$, CMe_3, C_9H_6N, CH=CHPh, CH=CHMe]

(iii) 55°C, 2 hours, toluene, [R=*p*-ClC_6H_4]

(iv) 1:2.5, room temp., [R=Me, Et, CMe_3, C_6F_5, $CH_2C_6F_5$]

(v) 2:1:2 for $[TiCl_3(O_2CR)]$:H_2O:THF (or $MeCO_2Et$), room temp., [R=Ph, Me, CMe_3]

(vi) 1:2 for $[\{TiCl_2(O_2CR)(RCO_2H)\}_2O]$:THF, toluene, room temp., 15 minutes [R=Me, Et, CMe_3]

(vii) 1:1 for $[\{TiCl_2(O_2CR)THF\}_2O]$:$H_2O$, toluene, room temp., 15 minutes [R=CMe_3]

(viii) Toluene, 110°C, R=Me, Et, CMe_3]

(ix) 1:2.5, [R=Et (60°C), *para*-benzoate (100°C)]

(x) Light petroleum ether, [R=Et (60°C), CMe_3 (40°C)]

(xi) Toluene, 110°C, 2 hours, [R=C_6F_5, $CH_2C_6F_5$]

(xii) 1:2, [R=Ph], 100°C

(xiii) 1:3, toluene, 110°C, [R=C_6F_5, $CH_2C_6F_5$]

Figure 8.1 Summary of the reactions of $TiCl_4$ with carboxylic acids.

time, an increase in temperature or possibly a higher ratio of the acid to titanium, is needed for further reaction to occur. *Para*-benzoic acids have previously been shown to also form compounds of the formulation $[Ti_3O_2Cl_3(O_2CR)_5]$ but at higher temperatures of 100°C.[192] However initial studies concerning the *ortho* and *meta* substituted acids have shown that they do not give species of this stoichiometry, their steric effect giving species of a different formulation.[188]

The co-ordinated acid ligands in $[\{TiCl_2(O_2CR)(RCO_2H)\}_2O]$ (R=Me, Et, CMe_3) have been shown to be replaceable with THF molecules to give species of the type $[\{TiCl_2(O_2CR)THF\}_2O]$ which, in contrast to the former compounds, are stable on refluxing in toluene solution. This stability is not surprising as there is not an excess of carboxylic acid ligands which may contribute to the oxo bridge and the formation of acid chloride. The compound $[\{TiCl_2(O_2CCMe_3)THF\}_2O]$ undergoes hydrolysis with the elimination of HCl to give the tetrameric species $[\{TiOCl(O_2CCMe_3)THF\}_4]$. Although not prepared for this thesis, similar derivatives for acetic and propanoic acid are also anticipated as forming from the corresponding binuclear THF adducts.

For each of the seven titanium carboxylate species which have been fully structurally characterised for this thesis, the bridging co-ordination mode is predominant. Unidentate ligation has only been proposed for the compound $[\{TiCl_2(O_2CCH_2C_6F_5)(C_6F_5CH_2CO_2H)\}_2O]$ Form B where a high value of $\upsilon(COO)_{asym}$ ($1687cm^{-1}$) is found. Throughout this thesis IR analysis of the compounds has been a useful indication of the co-ordination mode of the carboxylate ligands, and the findings of Deacon and Phillips for acetate and trifluoroacetate compounds have been found to hold for other carboxylate ligands, both alkyl and aromatic. During the course of this work we have not found any example of the bidentate chelating mode to the titanium centre, presumably due to the greater strain of the four membered ring which forms between the ligand and the metal.

At present titanium carboxylate chemistry still has a great scope for expansion. With a larger number of differing characterised carboxylate compounds it would then be

possible to establish trends on substituting one carboxylate ligand for another. However, some observations may be noted from the work carried out so far:

(i) Strong acids such as $C_6F_5CO_2H$ and $C_6F_5CH_2CO_2H$ do not form 1:1 species at room temperature or even at -50°C but react, even when $TiCl_4$ is in excess, to give compounds of the type $[\{TiCl_2(O_2CR)(RCO_2H)\}_2O]$. This may possibly be due to the carboxylate carbon of these stronger acids being more δ+ve and therefore susceptible to attack by a chloride ion to produce acid chloride and subsequently an oxo bridge. However with the presence of an etheral group, as in $C_6F_5OCH_2CO_2H$, the etheral oxygen takes up the sixth co-ordination site to give $[\{TiCl_2(O_2CCH_2OC_6F_5)\}_2O]$.

(ii) The alkyl acids (R=Me, Et, CMe_3) react with $TiCl_4$ in a 1:1 or 1:2.5 ratio and may give oxo species of the type $[Ti_3O_2Cl_3(O_2CR)_5]$ at 40°C (R=CMe_3) or 60°C (R=Et). The *para*-benzoic acids (R=*p*-XC_6H_4, X=F, Cl, Br) produce $[Ti_2Cl_7(O_2CR)(RCO_2H)]$ at 0-25°C with an equivalent ratio of $TiCl_4$.[170] However, no species have so far been isolated utilising 1:2 or 1:2.5 reactant ratios at room temperature, but as similar oxo species corresponding to $[Ti_3O_2Cl_3(O_2CR)_5]$ have been identified at 100°C then it appears very likely that $[\{TiCl_2(O_2CR)(RCO_2H)\}_2O]$ may also exist.

(iii) Strong acids such as $C_6F_5CO_2H$ and $C_6F_5CH_2CO_2H$ react at high temperatures with $TiCl_4$ to give products containing no chlorine atoms through the formation of hydrogen chloride and the respective acid chloride. However again $C_6F_5OCH_2CO_2H$ is an anomaly to this as the product $[Ti_3O_2Cl_4(O_2CCH_2OC_6F_5)_4]$ appears to be formed.

(iv) In general for the reaction of $TiCl_4$ with carboxylic acids, the formation of oxo bridges increases with an increase in the reaction temperature and / or an increase in the acid strength.

The area of titanium carboxylate species is clearly very large. The compounds of bulky, sterically hindered acids such as the *ortho*- and *meta*- substituted benzoic acids need to be structurally characterised along with those of the stronger alkyl acids such as trifluoro- and trichloroacetic acids. The presence of etheral oxygen atoms or further functional groups in carboxylic acids which may additionally co-ordinate to the titanium could also be further explored. Additionally, as a comparison to the monocarboxylate systems, some brief work has been carried out within these laboratories concerning the reaction of $TiCl_4$ with dicarboxylic acids such as succinic acid ($HO_2C(CH_2)_2CO_2H$) and glutaric acid ($HO_2C(CH_2)_3CO_2H$). The results obtained suggested that polymerisation was occuring and even on utilising high dilution techniques, highly insoluble products were produced. However, with careful control of the reaction conditions such as temperature and concentration, it may be possible to isolate mononuclear or binuclear species. It would therefore be interesting to study these reactions in greater detail as these types of carboxylate anions have the ability to behave as tetradentate donors.

A wide research area still available is the reaction of $TiCl_4$ with carboxylic acids in the presence of an alcohol such as ethanol, to produce mixed alkoxide-carboxylate species as described in Chapter 5. Again the effect of acid strength, sterically hindered ligands and temperature could be investigated in order to prepare new polynuclear titanium carboxylate compounds.

The chemistry of aluminium carboxylate species has only been introduced briefly in this thesis but we have already seen that these compounds may be prepared and isolated conveniently in high yield. The species $[AlCl_2(O_2CR)]$ (R=Et, CMe_3) were able to be isolated as crystalline compounds, but X-ray diffraction studies for the trimethylacetate derivative were unsuccessful due to weakly diffracting crystals. This area of aluminium chemistry has been explored previously but no X-ray structural evidence for the proposals has been reported. In addition to these simple aluminium species, it may be possible that reaction of compounds of the type $[\{TiCl_2(O_2CR)(RCO_2H)\}_2O]$ with $AlCl_3$ could produce

heterobimetallic aluminium-titanium carboxylate species through the elimination of hydrogen chloride.

Finally, the results of the Ziegler-Natta catalytic experiments have shown that the activity of titanium carboxylate species increases on supporting the compounds on an inert support such as magnesium chloride. As only a small number of compounds have been tested no conclusions concerning the effect of the differing carboxylate ligands may be drawn at present. However it does appear that as expected, the presence of *cis* chlorine atoms in the molecule is a requirement for this type of active catalytic precursor. Unfortunately, the polymers which were produced in these catalytic tests were not subsequently analysed for their stereoregularity and therefore the effect of the use of titanium carboxylate species on stereospecificity could not be examined.

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APPENDIX

Crystal data for those compounds which are described in this thesis are given below. Atomic co-ordinates, bond lengths, bond angles, and thermal parameters have been deposited with the Cambridge Crystallographic Data Centre.

(i) **$[\{TiCl_2(O_2CEt)(EtCO_2H)\}_2O]$**

$C_{12}H_{22}Cl_4O_9Ti_2$, M=547.87, Monoclinic, space group C2/c, a=34.128(11), b=8.291(3), c=16.503(6)Å, β=104.61(3)°, U=4518.6Å^3, Z=8, D_c=1.61gcm^{-3}, Mo-K_α radiation, λ=0.71073Å, μ(Mo-K_α)=1.22mm^{-1}, T=220K, R=0.023 for 3977 unique observed (I/σ(I)≥2.0) reflections.

(ii) **$[\{TiCl_2(O_2CCMe_3)(Me_3CCO_2H)\}_2O]$**

$C_{20}H_{34}Cl_4O_9Ti_2$, M=660.1, Monoclinic, space group $P2_1$, a=10.618(10), b=12.900(9), c=12.076(7)Å, β=92.05(6)°, U=1653(2)Å^3, Z=2, D_c=1.33gcm^{-3}, Mo-K_α radiation, λ=0.71069Å, μ(Mo-K_α)=0.84mm^{-1}, T=290K, R=0.023 for 1267 unique observed (I/σ(I)≥2.0) reflections.

(iii) **$[\{TiCl_2(O_2CCH_2OC_6F_5)THF\}_2O]$**

$C_{24}H_{20}Cl_4F_{10}O_9Ti_2$, M=896.01, Monoclinic, space group C2/c, a=19.012(3), b=6.799(2), c=25.601(3)Å, β=92.04(3)°, U=3307.15Å^3, Z=4, D_c=1.80gcm^{-3}, Mo-K_α radiation, μ(Mo-K_α)=8.9cm^{-1}.

(iv) **$[\{TiOCl(O_2CCMe_3)THF\}_4]$**

$C_{36}H_{68}O_{24}Cl_4Ti_4$, M=1218.3, Orthorhombic, space group Pbca, a=13.084(9), b=18.863(15), c=21.484(15)Å, U=5302Å^3, Z=4, D_c=1.53gcm^{-3}, Mo-K_α radiation, λ=0.71069Å, μ(Mo-K_α)=0.86mm^{-1}, T=220K, R=0.056 for 2497 unique observed (I/σ(I)≥2.0) reflections.

(v) **$[Ti_3O_2Cl_3(O_2CEt)_5]$**

$C_{15}H_{25}Cl_3O_{12}Ti_3$, M=647.4, Monoclinic, space group $P2_1/n$, a=13.193(4), b=11.780(5), c=17.384(6)Å, β=95.67(3)°, U=2688Å^3, D_c=1.60gcm^{-3}, Mo-K_α radiation, λ=0.71069Å, μ(Mo-K_α)=1.22mm^{-1}, T=290K, R=0.048 for 2881 unique observed ($I/\sigma(I)\geq 2.0$) reflections.

(vi) **$[Ti_6O_4Cl_2(OEt)_6(O_2CCH_2C_6F_5)_8]$**

$C_{76}H_{46}Cl_2F_{40}O_2Ti_6$, M=2492.3, Triclinic, space group P1, a=11.406(3), b=12.080(3), c=18.106(6)Å, α=73.38(3), β=82.27(2), γ=83.97(2)°, U=2363.0Å^3, Z=1, D_c=1.75gcm^{-3}, Mo-K_α radiation, λ=0.71069Å, μ(Mo-K_α)=0.68mm^{-1}, T=290K, R=0.076 for 3879 unique observed ($I/\sigma(I)\geq 2.0$) reflections.

(viii) **$[\{TiO(O_2CC_6F_5)_2\}_8]$**

$C_{112}F_{80}O_{40}Ti_8.6C_7H_8$, M=3888.3+552.8 (=4441.1), Triclinic, space group P1, a=18.271(10), b=18.592(10), c=29.790(10)Å, α=102.85(4), β=98.31(4), γ=106.62(4)°, U=9216Å^3, Z=2, D_c=1.60gcm^{-3}, Mo-K_α radiation, λ=0.71069Å, μ(Mo-K_α)=0.48mm^{-1}, T=290K, R=0.140 for 6944 unique observed ($I/\sigma(I)\geq 2.0$) reflections.